A TEXT-BOOK

OF

Qualitative Analysis

OF

Inorganic Substances

BY

SYDNEY ALEXANDER KAY, D.Sc.

Lecturer in Chemistry, University of Edinburgh

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QUALITATIVE ANALYSIS
OF INORGANIC SUBSTANCES

PREFACE

IN teaching qualitative analysis to large classes of students, it is a common experience to find that so much of the available time is occupied in giving verbal instruction in the essential details of analytical technique that too little remains for the discussion of the underlying chemical principles.

In this little book analytical procedure is described somewhat minutely, in order that the student who follows the instructions will not require constant supervision in the laboratory, and that the teacher will be free to discuss with him the reactions upon which qualitative analysis is based. In the tutorial class—which ought, if possible, to form part of a course in analysis—more time should be available for the discussion of such subjects as chemical equilibrium, ionisation, relative strengths of acids and bases, hydrolysis of salts, all of which enter largely into the special problems of qualitative analysis.

To encourage proper methods of manipulation, and incidentally to effect economy not only of material but of time, special emphasis is laid upon the importance of using small quantities. Without guidance on this point, beginners almost invariably err in working with large beakers nearly full of solutions, instead of adjusting quantities and using methods such that all ordinary operations can be carried out in test-tubes, small porcelain basins, and (for hydrogen sulphide precipitations) small flasks. It is very desirable that students should be accustomed to carry out complete analyses with about one gram (in all) of material, and should be taught to use reagents in correspondingly small quantities

It is also good practice to provide for analysis substances containing quite a small proportion of certain constituents, *e.g.*, silver, manganese, carbonate, sulphate, cyanide, which, in small amounts, are commonly overlooked by a careless observer; and it is, of course, essential that the report of the analysis should clearly distinguish between the main constituents and those present in relatively small quantities, otherwise the analysis is inaccurate and misleading.

My thanks are due to Dr A. C. Cumming for the loan of blocks for Figs. 4 and 5; and I am deeply indebted to my colleague, Dr Leonard Dobbin, whose generous assistance, keen criticism, and friendly advice have been invaluable to me.

S. A. K.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH.
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QUALITATIVE ANALYSIS OF INORGANIC SUBSTANCES

THE method of analysis described in these pages is applicable to the following:—(1) mixtures of simple substances, mainly inorganic salts, oxides, acids, and bases, specially prepared for analytical practice; (2) metallurgical products, such as glasses and slags; (3) minerals; (4) alloys.

As no prescribed method of analysis can possibly deal with every situation that may arise in the course of the examination of a complex substance, the procedure is not to be regarded as a rigid system applicable without modification in all circumstances. Each new exercise invariably furnishes some new feature, and a beginner who follows the instructions, not in a mechanical manner but with a clear understanding of the chemical changes involved, should be able after some experience to devise methods of coping with difficulties as they arise. It is very desirable that a beginner should cultivate the habit of making careful notes of his own as to the best procedure in special cases. If these notes are arranged so as to be conveniently available, they will be found of great value for future reference.

NOTES ON APPARATUS AND METHOD OF WORK.

Test-tubes.—The best size for general use is 6 ins. × $\frac{3}{4}$ in. It is useful to note that 5 c.c. of liquid fills a test-tube of this size to a depth of about $\frac{3}{4}$ inch. Small test-tubes—4 ins. × $\frac{1}{2}$ in.—fitted as shown in Figs. 1 and 2, are occasionally useful. Several large tubes—so-called boiling-tubes—about 7 ins. × 1 in., should also be provided. A good test-tube brush is required for cleaning the tubes.

Wash-bottle.—A round flask, about 500 c.c., is best.

The jet should deliver a fairly fine stream of water. The wash-bottle should be kept ready for use filled with hot distilled water. String should be wound round the neck of the flask in order to protect the hand.

Funnels and Filter Papers.—The folded filter paper must be somewhat smaller than the funnel, and it must be folded so that it fits the funnel accurately. If the funnel angle is not exactly 60°, a paper folded in the usual way will not fit properly, but a cone of the appropriate size can

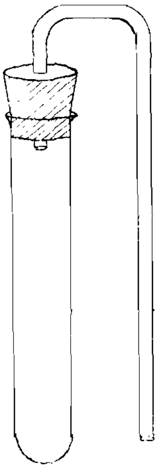

FIG. 1.

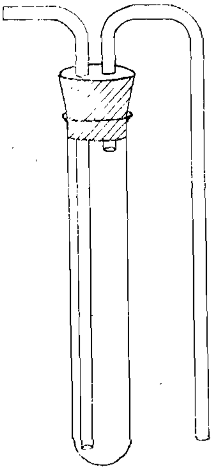

FIG. 2.

be obtained by allowing a certain overlap at the second fold. The folded paper is held in place in the dry funnel, which is then filled with water and the paper carefully pressed into contact with the funnel wall, especially round the top. If the paper fits properly, the funnel stem should fill with water and remain full after the excess of water has drained or been poured away.

Filter papers larger than 9 cm. in diameter should not be necessary. Small precipitates should be collected on correspondingly small filters.

Beakers.—Beakers are very seldom necessary in qualitative analysis; none larger than 100 c.c. need be provided.

Stirring Rods.—Glass rod, about 4 mm. diameter, is cut

into suitable lengths and the ends rounded in the Bunsen flame. Rods are required about 8 ins. long which will easily reach the bottom of a test-tube, and others, 3 to 4 ins. long, for use in basins. A rod pointed at one end is useful for piercing the apex of a filter. *Open glass tubes must not be used as stirring rods.*

Platinum Wires.—Two short pieces of platinum wire (one reserved for bead tests and the other for flame colorations) are mounted by sealing into glass rods. A cork is fitted on the other end of each rod, and the ends of the wires are kept immersed in hydrochloric acid in test-tubes.

Sublimation Tubes (Bulb-tubes).—Take a piece of soft glass tubing (at least 1 mm. thick in the wall), 6 ins. long

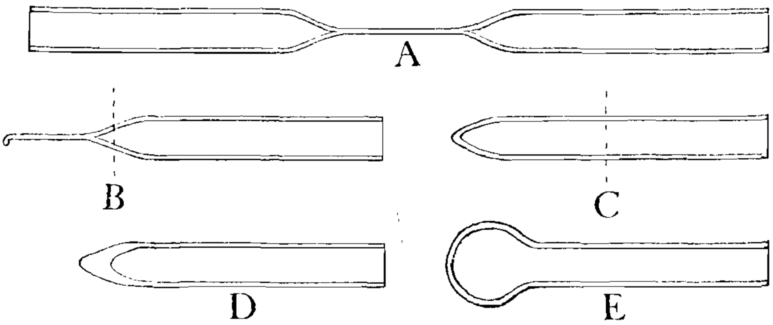

FIG. 3.

and ¼ in. internal diameter; hold it lightly between the thumb and finger tips of each hand, and *rotate it evenly* in the hottest part of the blowpipe flame so that the middle of the tube becomes uniformly heated. When the glass begins to soften, take care to turn the two ends evenly in order to avoid twisting the tube. When the glass has become quite soft, remove the tube from the flame, and gently pull the two ends apart (Fig. 3, A). Then separate the two ends by applying the flame at A and drawing the ends apart. Take one of the pieces and, by applying the flame at B, draw off the capillary, thus forming a closed tube (C). Now support the tube lightly at C between the thumb and finger tips of the left hand, rotate the tube with the right hand, and heat the closed end in the flame until

it becomes well softened and a blob of glass collects at the end, as shown at D. Remove the tube from the flame and at once blow the softened end into a small bulb. In blowing, a succession of short puffs is better than a continuous pressure. The finished tube should appear as shown at E, the bulb being about ½ in. diameter.

Economy of Substance and of Time.—The importance of using small quantities of the substance and of the needful reagents cannot be over-estimated. In analytical practice, the amount of substance available is sometimes strictly limited, and the beginner should note that in the case of a comparatively simple mixture *no more than* 1 *gram of the substance is necessary for a complete analysis.*

Economy of substance is not merely a question of expense; the main object aimed at is economy of time. It is obvious that much time will be saved in filtrations, washing of precipitates, evaporations, etc., if only test-tube quantities of liquids have to be dealt with instead of the beaker quantities which are often used. It is most important, however, when using a small quantity of the substance under analysis, to use the reagents in correspondingly small quantities, and to keep the total volume of liquid small by evaporating when necessary.

After a little experience, time can and must be economised by carrying on several operations alongside of one another. It is quite unnecessary to be idle, for example, while evaporation, filtration, etc., is going on, and practically every moment should be occupied in one way or another. Rapidity of work is next in importance to absolute certainty as to results.

Reagents and Reagent Bottles.—The possible presence of impurities in reagents should be constantly borne in mind. Sodium carbonate, for example, often contains traces of chloride and sulphate. Certain reagents, such as stannous chloride, hydrogen sulphide solution, ammonium sulphide, oxidise more or less rapidly and become useless in course of time. Stannous chloride solution keeps better if a piece of tin is placed in it.

The stoppers of reagent bottles should not be laid on the bench; if, occasionally, this cannot be avoided, the stopper

should be laid down inverted. After using a reagent, the bottle should be re-stoppered and at once replaced on the shelf in its proper position. *Reagent bottles must not be allowed to accumulate on the working bench.*

The use of hydrogen sulphide.—Hydrogen sulphide is a very poisonous gas. Severe headache and sickness result if air containing quite a small quantity of the gas is continuously breathed, and air containing about 1 part in 200 is said to be fatal. Momentary exposure to the undiluted gas may cause insensibility with extraordinary suddenness. It is, therefore, imperative that every care be taken to prevent contamination of the laboratory atmosphere with the gas and that the instructions regarding the use of the gas be closely followed.

Water dissolves about three times its volume of H_2S at ordinary temperatures, and it is sometimes more convenient to use a saturated aqueous solution of the gas—H_2S-water —instead of the gas itself. Unless the solution smells strongly of the gas, it is of no use as a reagent.

When it is desirable to avoid dilution of the solution under examination, the gas itself is used rather than H_2S-water, and the following instructions should be noted:—

1. The solution into which the gas is to be passed must *not* be placed in a beaker or a basin.

2. It is seldom proper to use a test-tube, unless the quantity of liquid is very small and only a few bubbles of gas are required.

3. The operation must be conducted in a draught-cupboard which, as far as possible, must be kept closed.

4. The following procedure must be adopted when it is necessary to saturate a solution with H_2S:—(*a*) Transfer the solution to a small flask (100 to 150 c.c.) fitted with a delivery tube which reaches almost to the bottom of the flask. Leave the cork quite loose in the flask, and bubble the gas through the solution for about one minute in order to displace the air in the flask. Push the cork firmly into place, leave the flask attached to the generator, and shake the flask vigorously at intervals during five to fifteen minutes until the solution is saturated with the gas. If the air in the flask has been completely displaced, the solution is known to

be saturated when the gas current stops in a few moments after shaking the flask vigorously. (*b*) Close the tap on the generator. (*c*) Remove the cork from the flask before disconnecting from the generator.

ANALYTICAL GROUPS AND GROUP REAGENTS.

Metallic Radicals.

In order to identify the metallic radicals present in a solution, it has been found convenient to separate them, first of all, into six groups. This is accomplished by means of certain group reagents, viz. :—

1. Hydrochloric acid.
2. Hydrogen sulphide (in presence of dilute hydrochloric acid).
3. Ammonia (in presence of ammonium chloride).
4. Ammonium sulphide.
5. Ammonium carbonate.

These group reagents are added to the solution in the order named, any precipitate that forms with a given reagent being separated by filtration before the reagent next in order is added. The six groups are as follows :—

Group I.—Silver Group. $Ag^{\cdot}$, $Hg^{\cdot}$, $Pb^{\cdot\cdot}$.

The chlorides of these radicals are insoluble in water, and they are precipitated, therefore, when hydrochloric acid is added to solutions of their salts (Note 1).

Group II.—Copper and Arsenic Group. $Cu^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, $Cd^{\cdot\cdot}$, $As^{\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Sn^{\cdot\cdot\cdot\cdot}$, $Sb^{\cdot\cdot\cdot}$.

The chlorides of these radicals are soluble in water (Note 1), and hydrochloric acid therefore gives no precipitates with solutions of their salts. The sulphides are insoluble in water and in dilute hydrochloric acid; hydrogen sulphide therefore precipitates the sulphides in presence of dilute acid.

Group III.—Iron Group. $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, ($Mn^{\cdot\cdot}$).

The chlorides of these radicals are soluble in water, and the sulphides are decomposed by dilute acid or in presence of water. The hydroxides are insoluble and are precipitated by ammonia (Note 2).

Group IV.—Zinc Group. $Zn^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$.

The chlorides of these radicals are soluble in water; the sulphides are decomposed by dilute acid; and the hydroxides are not precipitated by ammonia in presence of ammonium chloride (Note 2). The sulphides are insoluble in water and are precipitated by ammonium sulphide.

Group V.—Calcium Group. $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ba^{\cdot\cdot}$.

The chlorides and sulphides of these radicals are easily soluble in water and the hydroxides sparingly soluble, and hydrochloric acid, hydrogen sulphide, ammonia, and ammonium sulphide alike give no precipitates with solutions of their salts. The carbonates are insoluble and are precipitated by ammonium carbonate.

Group VI.—Magnesium and Alkali Metal Group. $Mg^{\cdot\cdot}$, $Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$.

These radicals are not precipitated by any of the group reagents. Magnesium hydroxide and magnesium carbonate are insoluble in water, and lithium carbonate is sparingly soluble, but they are not precipitated in presence of ammonium chloride (Note 2).

Notes.—1. Lead chloride is quite appreciably soluble in water and is not completely precipitated in Group I. by hydrochloric acid. It will be observed that lead, for this reason, appears in Group II. as well as in Group I.

2. Ammonium chloride is always added before the ammonia in order to prevent the precipitation in Group III. of manganese, magnesium, zinc, cobalt and nickel. The hydroxides of these radicals are precipitated (although incompletely) by ammonia, but not by ammonia in presence of ammonium chloride.

Ferrous salts are imperfectly precipitated by ammonia in presence of ammonium chloride, and in order to secure complete precipitation of iron, ferrous salts are oxidised to ferric salts by means of nitric acid before Group III. is precipitated.

Although manganous hydroxide is not precipitated in Group III., atmospheric oxidation of the ammoniacal solution results in the slow precipitation of manganic hydroxide, and if manganese is present it is always partially precipitated by ammonia together with ferric, chromic, and aluminium hydroxides.

Acidic Radicals.

The following is a list of the acidic radicals commonly met with:—

Carbonate.	Cyanide.	Arsenite.
Sulphide.	Ferrocyanide.	Arsenate.
Sulphite.	Ferricyanide.	Phosphate.
Thiosulphate.	Thiocyanate.	——
Nitrite.	——	Borate.
Hypochlorite.		Silicate.
——	Sulphate.	——
Fluoride.	Nitrate.	
Chloride.	Chlorate.	Acetate.
Bromide.	Chromate.	Oxalate.
Iodide.	Permanganate.	Tartrate.

Although the acidic radicals may be divided into Groups in accordance with their behaviour towards certain reagents (chiefly silver nitrate and barium nitrate), experience has shown that it is not advisable to attempt to separate them systematically as in the case of the metallic radicals. The results of certain preliminary and general tests are first carefully noted, and then special tests, or such special methods of separation as appear to be necessary, are used to identify individual acidic radicals.

SOLUTIONS FOR THE PRELIMINARY EXERCISES.

(See pp. 9-11.)

The preliminary exercises on the separation of metallic radicals ought to be carried out with solutions containing a known quantity of each metal, in order that the student in his subsequent work may be able to form a rough estimate of the amounts of the various constituents found in a given substance.

The solutions should contain 2 grams of each metal per litre, or 20 milligrams. in 10 c.c. In the case of lead, however, a higher concentration (50 milligrams in 10 c.c.) is required for precipitation in Group I., and the solution for the first preliminary exercise (p. 9) should therefore contain 3 grams of $AgNO_3$, 2·6 grams of $HgNO_3$, and 8 grams of $Pb(NO_3)_2$ per litre.

PRELIMINARY EXERCISES.

METALLIC RADICALS.

1. Precipitation and Analysis of Group I.

$Ag^{\cdot}$, $Hg^{\cdot}$, $Pb^{\cdot\cdot}$.

Use 10 c.c. of a solution containing silver, mercurous, and lead nitrates. To the cold solution add dilute HCl, little by little, with frequent shaking, as long as the precipitate continues to form. Shake well, and filter. Ascertain that precipitation has been complete by adding a few additional drops of HCl to the filtrate. When this is proved, neglect the filtrate, since the solution contains only the radicals of Group I.

Examine the precipitate as described on p. 46.

2. Precipitation and Analysis of Group II.

$Cu^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, $Cd^{\cdot\cdot}$, $As^{\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Sn^{\cdot\cdot\cdot\cdot}$, $Sb^{\cdot\cdot\cdot}$.

(1) Use 10 c.c. of a solution containing cupric, mercuric, lead, bismuth, and cadmium chlorides. Place the solution in a small flask (100 to 150 c.c.) and dilute to about 40 c.c. (Note the precipitation of BiOCl; it is readily converted into Bi_2S_3 by H_2S and in no way interferes with the course of the analysis). Saturate the solution with H_2S as described on p. 5. Keep it near the boiling-point for about half a minute, allow the precipitate to settle, and filter. Ascertain that precipitation has been complete by diluting further and passing more H_2S into the solution. When the filtrate gives no more precipitate with H_2S, neglect it.

Instead of using gaseous H_2S, the sulphides may be precipitated by means of H_2S solution, as follows:—To the solution in the flask, add 20 c.c. of H_2S solution and heat until boiling. Then add another 20 c.c. of H_2S solution and warm gently. Allow the precipitate to settle, and filter. Ascertain, as before, that precipitation has been complete by adding more H_2S solution to a portion of the filtrate, and, if necessary, treat the whole of the filtrate with more H_2S solution.

Examine the precipitate for the radicals of the Copper Group as described on p. 48.

(2) Use 10 c.c. of a solution containing cupric, arsenious, stannic, and antimonious chlorides. Precipitate the sulphides with H_2S as described on p. 5. Filter. Wash the precipitate with hot water containing a little H_2S.

Separation of the Copper and Arsenic Sub-Groups.—As described on p. 47, transfer the precipitate to a basin, add 20 c.c. of NaOH and 3 to 4 drops of yellow ammonium sulphide, warm gently for a few minutes, and filter.

Residue.—Examine for the radicals of the Copper Group as described on p. 48.

Filtrate.—Examine for the radicals of the Arsenic Group as described on p. 49.

3. Precipitation and Analysis of Groups III. and IV.

Group III. $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, ($Mn^{\cdot\cdot}$).
Group IV. $Zn^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$.

Use 10 c.c. of a solution containing the above radicals as sulphates or chlorides. To the solution contained in a boiling-tube, add about 5 drops of concentrated HNO_3 and boil for half a minute in order to oxidise $Fe^{\cdot\cdot}$ to $Fe^{\cdot\cdot\cdot}$. Add 2 grams of solid NH_4Cl and then NH_4OH until, after shaking, the mixture smells of NH_3. Boil for about a minute and make certain that NH_3 is present in the escaping steam. Filter.

Precipitate.—Observe its colour. Wash with hot water and examine for the radicals of the Iron Group as described on p. 50. Ascertain whether the original solution contains $Fe^{\cdot\cdot}$ or $Fe^{\cdot\cdot\cdot}$, or both, by testing small portions of the original solution with (*a*) $K_3Fe(CN)_6$ (*b*) KCNS.

Filtrate.—Transfer the filtrate to a small flask and saturate with H_2S as described on p. 5. Warm gently, and filter. Make certain that the filtrate will give no further precipitate with H_2S; when this is proved, neglect the filtrate.

Wash the precipitate and examine for the radicals of the Zinc Group as described on p. 52.

4. Precipitation and Analysis of Groups V. and VI.

Group V. $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ba^{\cdot\cdot}$.
Group VI. $Mg^{\cdot\cdot}$, $Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$.

Use 10 c.c. of a solution containing the radicals of Groups V. and VI. as chlorides. Add 5 c.c. of NH_4Cl, NH_4OH until alkaline, and then $(NH_4)_2CO_3$ as long as precipitate continues to form. Keep near the boiling-point for about a minute, and filter.

Precipitate.—Wash with warm water and examine for the radicals of the Calcium Group as described on p. 53.

Filtrate.—Examine for $Mg^{\cdot\cdot}$, $Li^{\cdot}$, $Na^{\cdot}$, and $K^{\cdot}$, as described on p. 55.

Test a small portion of the original solution for $NH_4^{\cdot}$ by boiling with NaOH and testing for NH_3 (or as described on p. 56).

5. The role of Ammonium Chloride in the Precipitation of Group III.

The precipitation of Group III. is effected by means of NH_4OH in presence of NH_4Cl, and it has been already explained (Note 2, p. 7) that the NH_4Cl is added chiefly in order to prevent the precipitation in Group III. of the hydroxides of $Mg^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Co^{\cdot\cdot}$, and $Ni^{\cdot\cdot}$. The hydroxides of these radicals are nearly insoluble in water and are precipitated (although incompletely) by NH_4OH alone, those of $Zn^{\cdot\cdot}$, $Co^{\cdot\cdot}$ and $Ni^{\cdot\cdot}$ being soluble in excess on account of the formation of complex ions of the general formula $M(NH_3)_x^{\cdot\cdot}$. In presence of NH_4Cl, however, NH_4OH produces no precipitates in any of the above cases. The explanation is as follows:—

NH_4OH is a *weak base*, i.e., it is only slightly ionised in aqueous solution and the concentration of OH' is low. The precipitation of a metallic hydroxide by NH_4OH will, in general, occur if the product of the concentrations of the metallic ion and the hydroxide ion exceeds a certain critical value—the so-called "solubility product" of the hydroxide. This condition is fulfilled in the case of magnesium hydroxide, for example, when NH_4OH is added to a solution

of $MgCl_2$. The equilibrium is determined by the following equations:—

$$(1)\ MgCl_2 \rightleftharpoons Mg^{\cdot\cdot} + 2Cl'.$$

$$(2)\ 2NH_4OH \rightleftharpoons 2OH' + 2NH_4^{\cdot}.$$

$$(3)\ Mg^{\cdot\cdot} + 2OH' \rightleftharpoons \underset{\text{(dissolved)}}{Mg(OH)_2} \rightleftharpoons \underset{\text{(solid)}}{Mg(OH)_2}.$$

If, however, an ammonium salt such as NH_4Cl, which is largely ionised, is added, the concentration of $NH_4^{\cdot}$ (equation 2) is thereby greatly increased and that of OH', therefore, correspondingly diminished, so that, notwithstanding a high concentration of $Mg^{\cdot\cdot}$, the product of the concentrations of $Mg^{\cdot\cdot}$ and OH' no longer attains the critical value necessary for precipitation of $Mg(OH)_2$.

The hydroxides of $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and $Cr^{\cdot\cdot\cdot}$, on the other hand, are precipitated by NH_4OH in presence of NH_4Cl, notwithstanding the "suppression" of OH' by $NH_4^{\cdot}$, because, being less soluble than $Mg(OH)_2$, a much lower concentration of OH' is sufficient to bring the product of the concentrations of the metallic and hydroxide ions to the critical value.

Experiments.—(1) To 5 c.c. of $MgCl_2$ solution add NH_4OH until, after shaking, the mixture smells of NH_3. Filter. Add $(NH_4)_2HPO_4$ to the filtrate. The formation of a white, crystalline precipitate of $MgNH_4PO_4$ shows that the precipitation of $Mg(OH)_2$ by NH_4OH was incomplete.

(2) To 5 c.c. of $MgCl_2$ solution add NH_4OH in slight excess. Then add NH_4Cl. The precipitate dissolves, because the increased concentration of $NH_4^{\cdot}$ ion (added in the form of NH_4Cl) lowers or suppresses the concentration of OH' ion (with formation of unionised NH_4OH), and the equilibria represented by equations (2) and (3) above are displaced to the left.

(3) Add NH_4Cl and NH_4OH to each of the following solutions:—ferric, aluminium, chromic, zinc, manganous, cobalt, nickel, and magnesium sulphates or chlorides. Observe whether precipitates are obtained or not. Observe that although no precipitate forms immediately in the case of the solution containing the manganous radical, the ammoniacal solution becomes slowly turbid. The turbidity

is due to the precipitation of manganic hydroxide—$Mn(OH)_3$—or hydrous manganic oxide—$MnO(OH)$. The precipitation of manganese is thus not entirely prevented by NH_4Cl.

(4) To 50 c.c. of water add 1 c.c. of phenolphthalein solution[1] and divide into five portions:—

1st portion. Add 2 drops of NH_4OH. The red coloration shows the presence of OH′. Then add NH_4Cl solution drop by drop, until the coloration disappears. Then test the solution with red litmus paper. Also test the NH_4Cl solution with litmus.

2nd portion. Add 2 drops of NH_4OH and then solid $(NH_4)_2SO_4$.

3rd portion. Add 2 drops of NH_4OH and then solid NH_4NO_3.

4th portion. Add 2 drops of NH_4OH and then solid NaCl.

5th portion. Add 1 drop of NaOH solution and then solid NaCl.

The suppression of OH′ in NH_4OH solution is not obtained by adding NaCl instead of NH_4Cl. In the case of a *strong base* like NaOH, the concentration of OH′ is only slightly lowered by the addition of NaCl.

PRELIMINARY EXERCISES (*continued*).

ACIDIC RADICALS.

1. Sublimation Tube Test.

Make a number of sublimation tubes as described on p. 3. Heat very small quantities of each of the following substances in sublimation tubes as described on p. 22, and observe very carefully what occurs.

(*a*) Ferrous ammonium sulphate.
(*b*) Lead nitrate.
(*c*) Calcium acetate.
(*d*) Sodium sulphite.
(*e*) Sodium thiosulphate.
(*f*) Sodium potassium tartrate.

[1] One gram of the solid dissolved in 1 litre of 50 per cent. alcohol.

In the case of ferrous ammonium sulphate, the observations that may be made include the following:—

(1) Pale green substance becomes white.

(2) Water condenses. (Test with litmus paper.)

(3) NH_3 is liberated—odour and alkaline reaction. (Dry the tube inside with filter paper and heat further.)

(4) SO_2 is liberated—odour and acid reaction. (Dry the tube again, if necessary, and heat further.)

(5) White sublimate forms.

(6) The residue is dark brown and infusible.

Add dilute HCl to the cooled residues obtained in (*c*), (*d*), (*e*), and (*f*), and observe whether gas is evolved (CO_2 or H_2S).

2. Interaction of Substance with Dilute H_2SO_4 or HCl.

(See also p. 34.)

(*a*) In separate test-tubes warm 5 c.c. of dilute H_2SO_4 and 5 c.c. of dilute HCl. Note in each case whether the escaping vapour has any odour.

The object of this experiment is to demonstrate that the vapour formed by warming dilute hydrochloric acid has a slightly pungent (HCl) odour, which beginners sometimes mistake for that of sulphur dioxide or acetic acid. For this reason, dilute H_2SO_4 is usually the preferable reagent.

(*b*) Warm separately with 1 c.c. of dilute H_2SO_4 about 1 c.c. of each of the following dilute (approximately 0·5 per cent.) solutions:—Sodium sulphite (freshly made); sodium nitrite; bleaching-powder. Note very carefully the odour of the gas liberated in each case. Beginners often confuse the odours of Cl_2, SO_2, and NO_2, when only small quantities of these gases are present.

(*c*) Warm a few crystals of $KClO_3$ with 3 c.c. of dilute HCl. Note the colour and odour of the mixture of gases (Cl_2+ClO_2) liberated.

3. Interaction of Substance with Concentrated H_2SO_4.

(See also p. 35.)

In small, dry test-tubes warm a small quantity of each

of the following solids with not more than 1 c.c. of concentrated H_2SO_4:—

(*a*) Potassium bromide.
(*b*) Sodium chloride and potassium bichromate (mixed).
(*c*) Potassium chlorate (a very small quantity).
(*d*) Tartaric acid.

Note the colour, odour, etc., of the gases liberated. Very carefully compare the bromine evolved in (*a*) with the chromyl chloride formed in (*b*). (See also Note 5, p. 36.)

Use a very small quantity of $KClO_3$, as the gas that is formed (ClO_2) is explosive.

4. Identification of Iodide and Bromide.

Mix 1 c.c. each of potassium iodide and potassium bromide solutions, dilute to 10 c.c., and examine the solution for iodide and bromide by both methods described in para. (*a*), p. 63.

5. Identification of Chloride in presence of Bromide and Iodide.

Mix 1 c.c. each of potassium iodide, bromide, and chloride solutions, dilute to 10 c.c., and examine the solution for chloride as described in para. (*b*), p. 63.

Perform a similar experiment with a solution containing iodide and bromide only. No more than a trace of chloride (present as impurity) should be found.

6. Identification of Nitrate in presence of Bromide and (or) Iodide.

The presence of bromide or iodide interferes with the so-called "brown ring" test for nitrate, on account of the liberation of bromine or iodine. Nitrate may be identified in such mixtures by reduction to ammonia.

Mix about 2 c.c. of calcium nitrate solution (or a small crystal of KNO_3) with 10 c.c. of water. Add 2 drops of dilute H_2SO_4 and about 1 gram of zinc dust. Warm gently and set aside for about five minutes. Then add NaOH and

boil. The NH_3 that is liberated may be detected by smell and litmus paper. Care must be taken to hold the litmus paper outside the test-tube in order to prevent the NaOH touching it.

7. Identification of Fluoride.

When a fluoride is warmed with concentrated H_2SO_4, hydrogen fluoride is liberated. If the interaction takes place in a glass test-tube, the hydrogen fluoride attacks the glass, forming gaseous silicon fluoride, and the tube assumes a greasy appearance.

$$SiO_2+4HF = SiF_4+2H_2O.$$

The silicon fluoride may be identified by holding a drop of water on the end of a glass rod inside the test-tube: the water drop becomes coated with white silicic acid.

$$3SiF_4+4H_2O = H_4SiO_4+2H_2SiF_6.$$

(*a*) Warm a little CaF_2 with 2 c.c. of concentrated H_2SO_4 in a test-tube. Observe that the liquid behaves as if the glass were greasy. Test for SiF_4 as described above.

(*b*) **Glass Etching Test.**—Cover the convex surface of a watch-glass with a thin coating of paraffin wax by warming the glass and melting the wax upon it, and then allowing the wax to solidify. Cut a design through the wax by means of a metal point and place the watch-glass upon a leaden dish containing calcium fluoride and concentrated sulphuric acid. Warm the dish very gently, care being taken not to melt the wax (water may be placed in the watch-glass to prevent this happening). Remove the watch-glass after about five minutes, melt the wax and wipe the glass clean, when the design should be found etched upon its surface.

8. Identification of Borate.

Making use of borax, examine (*a*) the turmeric paper test, (*b*) the flame coloration test described on p. 67.

9. Silica and Silicates.

The only soluble silicates are those of the alkali metals. "Water-glass" is a syrupy solution of sodium silicate, Na_2SiO_3.

(1) Use a solution of sodium silicate (20 grams of water-glass in 100 c.c.) for the following experiments :—

(*a*) Test the solution with red litmus paper. To 10 c.c. add 5 c.c. of dilute HCl: the solution becomes milky, and in a few moments sets to a stiff jelly owing to the separation of gelatinous silicic acid.

(*b*) Dilute 2 c.c. of the solution to 10 c.c., and acidify with HCl. The silicic acid does not separate but remains in colloidal solution. Evaporate the solution to dryness (preferably on the steam-bath). During the evaporation silicic acid separates and is obtained as a white powder (mixed with NaCl). To the dry residue add dilute HCl and warm: the silicic acid is now insoluble in acid. Filter, wash the insoluble residue, and test it in a metaphosphate bead as described in (2).

(*c*) Dilute 2 c.c. of the solution to 10 c.c., and divide into two portions. To one portion add NH_4Cl; acidify the other portion with HCl, add NH_4OH until just alkaline, and boil. In each case silicic acid is precipitated and closely resembles $Al(OH)_3$ in appearance. In the systematic analysis for metallic radicals it is essential, for this reason, to remove silicic acid by evaporating the solution to dryness prior to the precipitation of Group III. (see p. 44).

(2) Fuse a minute particle of a silicate (*e.g.*, felspar) in a metaphosphate bead (p. 30). The silicate is decomposed and the basic oxides combine with and "dissolve" in the metaphosphate, but the silica (an acidic oxide) remains undissolved as a semi-translucent "skeleton" of the original particle of the silicate.

$$CaSiO_3 + NaPO_3 = NaCaPO_4 + SiO_2.$$

Silica and silicates may be identified in this way.

Systematic Analysis

The systematic examination of a substance is carried out in the following order :—

1. Preliminary examination.

2. Preparation of a solution of the substance and separation from any insoluble portion.

3. Systematic analysis of the solution for metallic radicals.

4. Examination for acidic radicals.

5. Examination of any insoluble portion.

All observations should be recorded during the course of the analysis and not after its completion. A *report* of each analysis, arranged under the main headings indicated above, is to be handed in for examination. The report should conclude with a summary of the results obtained. It is most important to state clearly which are the main constituents of the substance and which are present in relatively small quantity.

PRELIMINARY EXAMINATION.

The preliminary examination must never be omitted. It is important, not merely because it almost invariably results in the partial identification of the substance, but because it always gives information as to its general character and indicates what precautions (if any) are likely to be necessary in the preparation of the solution or in its subsequent analysis. If the preliminary tests indicate the presence of, for example, silicate, fluoride, or organic substances, the subsequent course of the analysis requires appropriate modification.

The preliminary tests, which are mainly dry-way tests, are as follows:—

(1) General appearance and physical characteristics.
(2) Sublimation tube test (effect of heat).
(3) Flame coloration test.
(4) Bead tests.
(5) Film tests.
(6) Blowpipe tests.
(7) Match tests.
(8) Interaction of substance with (*a*) dilute sulphuric acid, (*b*) concentrated sulphuric acid.

1. Physical Characteristics.

If the substance is liquid, note its colour, odour, and whether it is neutral, acid, or alkaline. Evaporate a small portion to dryness and examine any residue.

If the substance is a solid, note its colour, odour, and whether it is crystalline, amorphous, or metallic.[1] Try to observe whether the substance is homogeneous or is plainly a mixture. Individual particles possessing a distinctive colour or some other prominent feature may sometimes be picked out from a coarsely powdered mixture and examined separately with useful results.

[1] Some minerals have a metallic appearance, *e.g.* galena, pyrite ; and metals in a fine state of division are sometimes devoid of metallic lustre, *e.g.* zinc dust, ferrum redactum.

Colour.—Observation of the colour of a substance may give valuable hints as to the materials which are probably present or which must almost certainly be absent.

Colours of Salts and Oxides.

Black.

Cobalt oxide.
Cupric oxide.
Ferroso-ferric oxide.
Manganese dioxide.
Antimonious sulphide (natural).
Bismuth sulphide.
Cobalt sulphide.
Cupric sulphide.
Ferrous sulphide.
Lead sulphide.
Mercuric sulphide (precipitated).
Nickel sulphide.
[Carbon, charcoal, etc.]

Blue.

Many cupric salts.
Prussian blue.
Ultramarine.

Brown.

Ferric oxide.
Lead peroxide.
Ferric acetate.
Potassium ferricyanide (powdered).

Buff.

Lead oxide (litharge).
Manganous sulphide.
Manganous carbonate (white when freshly precipitated).

Green.

Chromic oxide.
Some chromic salts.
Cupric arsenite (Scheele's green).
Cupric chloride.
Ferrous sulphate.
Ferrous ammonium sulphate.
Many nickel salts.

Grey.

Nickel oxide.

Orange.

Antimonic sulphide.
Antimonious sulphide (precipitated).
Cadmium sulphide.
Lead chromate.
Several bichromates.

Pink.

Some cobalt salts.
Many manganous salts.

Purple.

Chrome alum.
Some other chromic salts.
Iron alum.
Potassium permanganate.

Red (Scarlet, etc.).

Chromic anhydride.
Cuprous oxide.
Lead oxide (red lead).
Mercuric oxide.
Mercuric sulphide (cinnabar: vermilion).
Mercuric iodide.
Mercurous chromate.
Some cobalt salts.

Yellow.

Mercuric oxide (precipitated).
Arsenious sulphide.
Cadmium sulphide.
Stannic sulphide.
Many chromates.
Some ferric salts.
Ferrous oxalate.
Lead iodide.
Potassium ferrocyanide.

Odour.—Ammonium carbonate, and other ammonium salts in admixture with various basic substances, undergo slow decomposition with evolution of ammonia. Some acetates alone, and acetates, generally, in admixture with acid salts, etc., give off more or less acetic acid; and the presence of cyanides, hypochlorites, acid sulphites, etc., may often be recognised by a characteristic odour.

Crushing and Grinding.—After the physical characteristics of a solid substance have been noted, it must be reduced to a moderately fine powder (unless it is already in that form) by grinding in a mortar. If the material is hard, it is first broken into a coarse powder in a steel "percussion" mortar, and is then ground in an agate mortar, in very small portions at a time. Refractory substances, such as glasses, slags, and many minerals, must be very finely powdered (see p. 75). Metals and alloys are dealt with as described on p. 73.

2. Sublimation Tube Test.

This is a most important test. *Provided it is carefully performed*, it gives much valuable information. Most of its value is lost, however, by a careless observer. Before proceeding with the test, have ready the following:—(*a*) A clean bulb-tube; (*b*) several pieces of filter paper folded or rolled so that they will enter the tube easily; (*c*) blue and red litmus paper, similarly folded.

Introduce enough of the substance to fill not more than one-third of the bulb, and carefully remove with filter paper any powder adhering to the narrow part of the tube.

Hold the tube in a horizontal position several inches above a small Bunsen flame, so as to warm the substance very gently. If water condenses in the cool part of the tube, ascertain its reaction to litmus paper, then heat a little more strongly; if more water appears, test with litmus paper again, and then remove the water with filter paper. When the tube is dry and no more water condenses, gradually heat more strongly until, finally, the glass begins to soften. Keep the tube and contents under very close observation throughout. The more important observations that may be made are indicated below.

(1) The colour of the substance changes.

(*a*) Temporary change of colour :—

Original colour.	Colour while hot.	
white	yellow	ZnO
white	yellow-brown	SnO_2
greenish-yellow	orange or reddish-brown	Bi_2O_3
buff	brown	PbO
red	chocolate	Pb_3O_4
red	black	HgO
crimson	yellow	HgI_2
scarlet	black	HgS

(*b*) Change of colour due to expulsion of water at a relatively low temperature from salt hydrates, *e.g.* :—

blue,	becomes	white :	$CuSO_4, 5H_2O$
green,	,,	brown :	$CuCl_2, 2H_2O$
green,	,,	yellow :	Nickel salts
crimson,	,,	blue :	$CoCl_2, 6H_2O$
pale brown,	,,	black :	$FeCl_3, 6H_2O$
pale green,	,,	white :	Ferrous salts

(*c*) Change of colour due to decomposition of salts at a relatively high temperature with formation of coloured residues, mainly oxides :—

Substance becomes

black, with odour of burnt organic matter (charring) :	Organic substances, especially tartrate.
black, no charring :	black oxide, *e.g.*, CuO, NiO, etc.
dark brown :	Mn_3O_4, CdO
reddish brown to black :	Fe_2O_3
brown, orange, or yellow :	see (*a*) above.

Note that blackening is not necessarily due to the charring of organic substances ; also that oxalates do not always char.

(2) **The substance melts**; the change is sometimes accompanied or followed by volatilisation or decomposition :—

(*a*) Many salts, *e.g.*, alkali hydrogen sulphates, chlorates, chromates, acetates, ammonium sulphate; some alkali and other halides (especially iodides); some nitrates.
(*b*) Some salt hydrates, especially nitrates, sulphates and chlorides.
(*c*) A few oxides, as PbO, Bi_2O_3, Sb_2O_3.
(*d*) Alkali hydroxides, and barium hydroxide.
(*e*) A few acids, as H_3BO_3, $(COOH)_2$, H_3PO_4.
(*f*) Some elements, as lead, sulphur, iodine.

(3) **Volatile products are given off.**

(*a*) Water vapour[1]: May be due to hygroscopic moisture; to decomposition of salt hydrates, acid salts, basic salts, ammonium salts. An alkaline reaction is usually due to the presence of ammonia derived from ammonium salts (or from some cyanogen compounds). An acid reaction indicates the presence of a volatile acid, as HCl, H_2SO_4, HNO_3, etc.
(*b*) Oxygen: From certain oxides and peroxides, as HgO, BaO_2; from chlorates, permanganates, bichromates, some nitrates, etc.
(*c*) Hydrogen: From formates (may be mixed with CO).
(*d*) Chlorine: From $AuCl_3$, $PtCl_4$, and some other chlorides; from chlorides in presence of an oxidising agent and an acid salt (or certain sulphates), as $NaCl + MnO_2 + FeSO_4$; also (mixed with oxygen) from some chlorates, as $Pb(ClO_3)_2$.
(*e*) Bromine: From bromides mixed with an oxidising agent and an acid salt.
(*f*) Iodine: From iodides mixed with an oxidising agent and an acid salt.

[1] If water is given off, the observation ought always to be reported.

(*g*) Nitrogen: From ammonium bichromate, ammonium nitrite, potassium ferrocyanide, etc. (nitrogen is not easily identified).

(*h*) Nitrous oxide: From ammonium nitrate, or other nitrate mixed with an ammonium salt.

(*i*) Nitrogen peroxide (mixed with oxygen): From nitrates and nitrites, except those of Na, K, NH_4, and Ba.

(*j*) Ammonia: From ammonium salts and some cyanogen compounds.

(*k*) Carbon dioxide: From carbonates (except alkali carbonates, $BaCO_3$, $SrCO_3$), oxalates, cyanates; from oxidation of carbonaceous substances, as tartrates, etc.

(*l*) Carbon monoxide: From formates, oxalates, tartrates, etc. (may be mixed with CO_2, CH_4, and H_2).

(*m*) Cyanogen: From cyanides of heavy metals, as $Hg(CN)_2$; from ferricyanides (mixed with N_2); from thiocyanates of heavy metals (mixed with CS_2 and N_2).

(*n*) Carbon disulphide: From thiocyanates of heavy metals [mixed with $(CN)_2$ and N_2].

(*o*) Sulphur dioxide: From acid sulphites, some sulphates and thiosulphates; from the oxidation of sulphides and thiocyanates.

(*p*) Hydrogen sulphide: From hydrosulphides and moist sulphides; from sulphites and thiosulphates in presence of water.

(*q*) Phosphine: From phosphites and hypophosphites.

(*r*) Halogen acids, nitric acid, acetic acid, and other volatile acids: From chlorides, nitrates, acetates, etc., in presence of acid salts, easily decomposable sulphates, etc.

(*s*) Silicon fluoride and boron fluoride: From fluorides in admixture with silica or a silicate (glass) or with borate, in presence of certain acid salts, etc.

(*t*) Chromyl chloride: From chromate or bichromate in admixture with a chloride, in presence of certain acid salts, etc.

(*u*) Acetone (burns with luminous flame; characteristic odour): From acetates, usually accompanied by charring.

(*v*) Inflammable vapour (luminous flame; odour of burnt sugar): From tartrates (charred residue).

(4) **A sublimate forms.**

(*a*) White: $HgCl_2$ (fusible), $HgCl$ (infusible), As_2O_3 (often crystalline), NH_4Cl or other NH_4 salt.

Distinguish between Hg, As, and NH_4 compounds as follows:—Mix about 10 mgrms. of the substance with 4 to 5 times as much dry Na_2CO_3 and a little charcoal. Heat the mixture in a bulb-tube, very gently at first, and then, after removing with filter paper any moisture that condenses, heat more strongly.

Hg, As, and NH_4 compounds give, respectively, a grey metallic sublimate (globules on rubbing); a black sublimate with metallic lustre, accompanied by a garlic-like odour; no sublimate, but odour of NH_3.

(*b*) Grey, metallic lustre, globules on rubbing: Hg.

(*c*) Yellow, becoming red on rubbing: HgI_2.

Yellow and yellow-brown drops: Sulphur (from thiosulphates, polysulphides, and some sulphides. *e.g.* FeS_2).

(*d*) Reddish-yellow: As_2S_3.

(*e*) Black, with metallic lustre: As.

Black, crystalline, violet vapour: Iodine.

3. Flame Coloration Test.

Mix a small quantity of the substance with one drop of concentrated hydrochloric acid on a watch-glass and hold some of the mixture, taken up on the looped end of a platinum wire, first in the lower part of the Bunsen flame where the temperature is relatively low, and afterwards gradually raise it to the hottest part of the flame (Fig. 4, p. 29). Observe the flame closely and continuously so long as any coloration lasts.

Dip the wire into the mixture again and repeat the test;

examine the flame coloration through blue glass and also with a hand spectroscope.[1]

Characteristic flame colorations may be obtained as follows :—

Bright yellow, persistent .	Sodium.
Pale violet, somewhat fleeting	Potassium.
Crimson, somewhat fleeting .	Lithium.
Crimson, somewhat persistent	Strontium.
Brick-red, duration variable .	Calcium.
Pale green, persistent . .	Barium.
Pale green, fleeting . .	Manganese.
Bright green or blue . .	Copper.
Livid blue, fleeting . .	Lead, Arsenic, Antimony.

The duration of flame colorations depends primarily on the rapidity with which the salt volatilises in the flame, and for a given metal it varies with the nature and amount of the salt present, with the temperature of the flame, etc. Some non-volatile salts, *e.g.* $BaSO_4$, $Ca_3(PO_4)_2$, give little or no flame coloration although previously moistened with HCl. If $BaSO_4$ is reduced to BaS by heating in the reducing flame and then moistened with HCl, a good flame coloration can be obtained.

Yellow Coloration. — This is a very delicate test for sodium. Unless the coloration is bright and fairly persistent, it is probably due to only a small amount of sodium. In the spectroscope the characteristic yellow line is invariably seen, although the amount of sodium present may be so minute that all other methods fail to detect it.

The sodium flame coloration is not visible through blue glass. (Two or three pieces, held together, may be required to cut off the yellow coloration completely.)

Violet Coloration.—The flame coloration due to potassium appears red (or violet-red) through blue glass. It is there-

[1] In using the spectroscope care must be taken to keep the inner blue cone of the Bunsen flame below the line of vision, otherwise lines due to the carbon spectrum of the Bunsen flame may be seen. Spectroscopic observations are best made against a dark background, or in a darkened room.

fore possible to detect potassium in presence of sodium by this means. In the hand spectroscope the characteristic red and violet lines at the extreme ends of the spectrum are not easily seen.

Crimson and Red Colorations.—The brilliant lithium flame coloration is usually of short duration, as lithium chloride volatilises quickly and completely, whereas the strontium flame is fairly persistent. The orange-red coloration due to calcium often appears as momentary flashes, which are repeated each time the wire is moistened with HCl and reheated. The lithium, strontium, and calcium flame colorations are *not* visible through deep cobalt-blue glass.

The spectroscope affords a ready means of distinguishing the above red flame colorations. The following are the prominent lines in each spectrum:—

Li: *One* very brilliant red line.

Sr: A bright orange and several red lines; and a characteristic blue line (not very easily seen).

Ca: A bright green and a bright red line (about equidistant from the Na line).

Green Coloration. — The apple-green colorations due respectively to barium and manganese closely resemble one another. The barium coloration is, however, very persistent, whereas that due to manganese quickly vanishes but reappears momentarily each time the wire is moistened with HCl and reheated.

Blue Coloration.—The livid blue (grey-blue) colorations due to some lead, arsenic, and antimony compounds are fleeting, and are usually accompanied by a white fume of the oxides.

4. Bead Tests.

With Borax.—This test should be tried if the substance is coloured, or if, in the case of a white substance, a coloured residue is obtained in the sublimation tube.

Dip the end of a hot platinum wire (not looped) into powdered borax, and heat the borax that adheres to the wire so as to form a transparent, colourless bead about 1·5 mm. in diameter. Bring the moistened bead into contact

with some very small particles of the substance, and heat the bead and substance for not less than thirty seconds in the oxidising flame (the outer border of a non-luminous flame, Fig. 4). Withdraw the bead from the flame and observe its colour while it is hot (not red-hot) and after

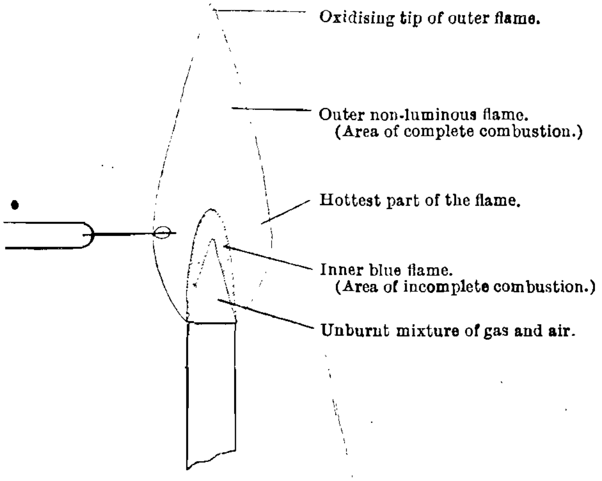

FIG. 4.

it has become cold. Then heat the bead in the reducing flame[1] (Fig. 5) and again observe its colour.

The following beads are characteristic:—

Blue in both flames:	Co
Green in both flames:	Cr
Amethyst in oxidising flame: / Colourless in reducing flame:	Mn
Reddish-brown in oxidising flame: / Grey and turbid, or colourless, in reducing flame:	Ni
Brown (hot), yellow (cold), in oxidising flame: / Olive green in reducing flame:	Fe
Green (hot), blue (cold), in oxidising flame: / Brown-red and opaque, or colourless, in reducing flame:	Cu

[1] A suitable reducing flame is obtained by adjusting the gas supply to give a 2 in. flame and reducing the air supply until the tip of the inner cone just becomes luminous. The bead is heated in the luminous tip. A metal shield to steady the flame is desirable.

If the bead appears black and opaque, too much substance has been used, and a fresh bead must be made. The coloured beads are metaborates or orthoborates:—

$$Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3.$$
$$B_2O_3 + CuO \rightarrow Cu(BO_2)_2.$$
$$NaBO_2 + CuO \rightarrow NaCuBO_3.$$

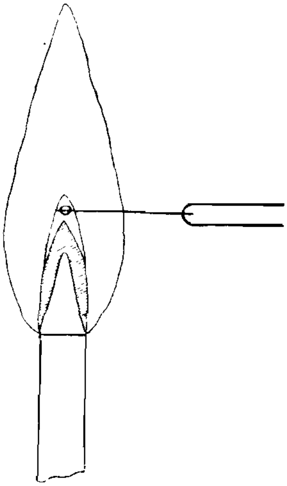

FIG. 5.

With Microcosmic Salt.—For silica or a silicate.

Make a bead of sodium metaphosphate ($NaPO_3$) by heating microcosmic salt on a platinum wire. Heat a small quantity of the substance in the bead. Basic oxides "dissolve" in the metaphosphate—giving transparent beads generally similar to those obtained with borax—but SiO_2 is not attacked and gives a turbid bead. A silicate is decomposed and the basic oxides dissolve, but the SiO_2 remains undissolved as a semi-translucent "skeleton" of the original particle of the silicate. Some silicates, however, leave no "skeleton."

SnO_2 dissolves very slowly in the bead and may be mistaken for SiO_2.

With Sodium Carbonate.—Fuse some Na_2CO_3 on a looped platinum wire so as to obtain, when cold, an opaque,

white bead. Take up with the bead a small quantity of the substance together with a small crystal of KNO_3, and heat in the oxidising flame.

A green bead (manganate) indicates Mn.
A yellow bead (chromate) indicates Cr.

Dissolve the bead in water, filter if necessary, and test for sulphate. A positive result indicates that sulphur, free or combined, is present in the substance.

5. Film Tests.

....eful preliminary test is here briefly described.

Take up a small quantity of the substance on the moistened end of an asbestos thread. Heat it in the reducing flame (Fig. 5), and hold a glazed porcelain basin containing a little water close above the asbestos. If a black or grey metallic film condenses on the basin, treat the film with a drop of cold, dilute HNO_3. Results may be obtained as follows:—

Arsenic, Antimony films . . . . Scarcely attacked by HNO_3.
Bismuth, Mercury films . . . . . Slowly dissolved by HNO_3.
Lead, Cadmium, Zinc films . . . Instantly dissolved by HNO_3.

If the film is not soluble in HNO_3, treat it with bleaching solution:—

Arsenic film . . . . . Instantly dissolved.
Antimony film . . . Very slowly attacked.

Full information regarding film tests is given in Dobbin and Marshall's *Salts and their Reactions.*

6. Blowpipe Tests.

In a shallow cavity (scooped out with the edge of a sixpenny piece) on a charcoal block, heat some of the

substance in the blowpipe flame.[1] Try the effect both of the reducing and of the oxidising flame.

With the reducing flame, the formation of an incrustation (an oxide film) on the charcoal may be observed, as follows:—

(1) *White incrustation.*

Very easily volatilised: garlic-like odour .	Arsenic.
Deposited close to cavity: less easily volatilised	Antimony.
Pale yellow when hot	Zinc.

(2) *Yellow incrustration.*

Lemon-yellow (hot), pale yellow (cold) .	Lead.
Orange (hot), yellow (cold)	Bismuth.

(3) *Red-brown incrustation* . . . . . Cadmium.

Reduction to the metallic state may also occur, but the match test (p. 33) is a more efficient method of observing this reaction.

With the oxidising flame, observe whether the substance decrepitates, deflagrates, fuses, or volatilises; note also the nature and colour of any residue. If the residue is white, infusible, and luminescent in the flame (CaO, SrO, BaO, MgO, Al_2O_3, ZnO, SiO_2, etc.), moisten it with a drop of cobalt nitrate and reheat. A coloured mass may remain, as follows:—

Green . .	Zinc.
Blue . .	Aluminium (also phosphates, arsenates, borates, and silicates).

[1] Adjust the Bunsen burner to give a medium-sized *luminous* flame (air-holes completely closed).

To obtain an oxidising flame, hold the nozzle of the blowpipe *within* the Bunsen flame and blow somewhat strongly so as to produce a well-defined non-luminous jet of flame; heat the substance near the extreme tip of this flame.

To obtain a reducing flame, hold the blowpipe nozzle just outside the Bunsen flame and blow gently so as to produce a slightly luminous jet of flame; heat the substance at the tip of the *inner* flame.

The maintenance of a steady supply of air from the mouth cavity (cheeks expanded)—meanwhile breathing freely through the nose—is a knack that is easily acquired with practice.

7. Match or Charcoal-stick Tests.

Remove the head from an ordinary large wooden match (or obtain a similar splinter of wood). Heat a corner of a piece of washing-soda and cover about two-thirds of the match with the molten salt. Heat gently until dry, and apply another coat of sodium carbonate. Then heat the match cautiously in the flame until it begins to char.

On a watch-glass mix a small quantity of the substance with a drop of melted sodium carbonate. Take up the mixture on the end of the match, and heat in the reducing flame (Fig. 5) for 2-3 minutes. Cool the end of the match in the unburned gas at the base of the flame, and then crush it gently under water in an agate mortar. Carefully wash away the charred remains of the match, and examine any heavier particles that remain. The following may be present in the residue:—

White metallic beads (malleable) .	Pb (marks paper), Ag, Sn.
White metallic beads (brittle) . .	Bi, Sb.
Red beads or sintered mass (malleable)	Cu.
Grey or black powder (magnetic) .	Fe, Ni, Co.

Fine particles of Fe, Ni, or Co are not recognisable by their appearance, but may be identified and withdrawn by means of a magnetised knife-blade which is brought into contact with the residue under water.

The beads of Sn are very small but may be rendered evident as characteristic metallic streaks by rubbing the wet residue somewhat heavily with the pestle.

"*Hepar*" *test.*[1]—The presence of sulphur compounds in the substance may be recognised by placing a portion of the original fused mass on a silver coin and adding a drop of water, when a brown or black stain will appear. (Iodide may cause a dark stain unless the coin is freshly polished.)

[1] So-called because hepar sulphuris or liver of sulphur (a pharmacopœial preparation containing potassium polysulphide) also gives this reaction.

8a. Interaction of Substance with dilute H_2SO_4.

In a *small* test-tube mix a small quantity of the substance with 1 to 2 c.c. of dilute H_2SO_4. Observe carefully whether, in the cold or on warming, the interaction gives rise to any recognisable gaseous product. Evolution of the following gases may be observed :—

		Recognised by
CO_2 (with effervescence) .	From carbonate .	Lime-water test (Note 1).
Cl_2 (in the cold) . .	From hypochlorite .	Odour, and bleaching action.
H_2S (may show effervescence)	From sulphide .	Odour, and lead acetate paper (Note 2).
SO_2 (may effervesce) .	From sulphite . .	Odour, and chromic acid paper.
SO_2 (with precipitation of sulphur)	From thiosulphate .	" " "
NO_2	From nitrite . .	Colour, odour, and KI paper.
HCN (in the cold) . .	From cyanide .	Odour, and "Prussian-blue" test (Note 3).
(on warming) .	From soluble ferro- and ferri-cyanide	Odour, and "Prussian-blue" test (Note 3).
O_2	From peroxide (Na_2O_2, BaO_2)	Glowing splint.
Acetic acid . . .	From acetate . .	Odour.

Notes.—1. The presence of a very small quantity of carbonate is most readily detected by dropping a little of the substance into two drops of cold, concentrated HCl in a small test-tube. The evolution of a minute amount of CO_2 should be visible, and effervescence may be audible if the mouth of the test-tube is held close to the ear. In testing for CO_2 with a drop of lime-water on a glass rod, care must be taken that minute particles of acid solution are not spirted into the lime-water.

2. Some sulphides (*e.g.*, FeS_2, HgS) are not decomposed by dilute H_2SO_4. If, however, a little zinc dust is added with the acid, H_2S is liberated on warming.

3. HCN is very poisonous, and care must be taken not to inhale more than a minute quantity.

A sensitive test for HCN is made as follows:—On a glass rod (or a looped platinum wire) hold a drop of NaOH solution for about a minute in the vapour to be tested. Transfer the drop to a white porcelain surface, add (with a pointed glass rod) a droplet of $FeSO_4$ solution, and then add a drop of HCl: a blue coloration ("Prussian blue") shows that HCN was present.

4. When a mixture of gases is evolved, *e.g.* from sulphite and

carbonate, their identification may require care or special methods. If SO_2 is liberated, it masks the lime-water test for CO_2. To prevent this, the substance may be mixed with $K_2Cr_2O_7$ before warming with dilute H_2SO_4, when the sulphite is oxidised and no SO_2 is evolved.

5. Chlorine, bromine, or iodine may be liberated from a chloride, bromide, or iodide in presence of an oxidising agent.

6. If the substance is warmed with dilute HCl (instead of H_2SO_4), there may be evolved, in addition to the gases enumerated above—

Cl_2, by oxidation of the HCl in presence of an oxidising agent, such as a dioxide (MnO_2), chromate, permanganate.

Cl_2+ClO_2 (recognised by odour and green colour), in presence of chlorate.

Some gaseous HCl (slightly pungent odour) will also be present in the escaping vapour, and for this reason dilute H_2SO_4 is preferable when testing for sulphite, acetate, etc.

8b. Interaction of Substance with Concentrated H_2SO_4.

In a *small* (4 in. × ½ in.) *dry* test-tube place a small quantity of the substance, and add carefully 3 to 4 drops of concentrated H_2SO_4: observe any visible interaction, and then warm very gently. Add a little more acid, but not more than 1 c.c. in all, and warm again (but do not boil). If *chlorate* is thought to be present, very little of the substance should be used. In addition to the gases liberated by dilute H_2SO_4, evolution of the following may be observed:—

Hydrogen chloride (fuming, colourless): from chloride (Note 1).

Chlorine: from chloride in admixture with an oxidising agent, as nitrate or peroxide.

Hydrogen bromide (fuming) and **bromine** (brown), with SO_2: from bromide (Note 2).

Iodine, with SO_2 or H_2S: from iodide.

Nitric acid vapour and **nitrogen peroxide** (brown): from nitrate.

Chlorine dioxide (with crackling or explosion): from chlorate.

Hydrofluoric acid and **silicon fluoride** (tube appears greasy): from fluoride.

Carbon monoxide (inflammable; blue flame): from ferro- and ferri-cyanide.

Carbon monoxide and **dioxide**: from oxalate (Note 3).

Sulphur dioxide (with CO and CO_2, and charring): from tartrate (Note 4).

Chromyl chloride (CrO_2Cl_2; greenish-yellow vapour, condensing to red drops): from chromate or bichromate in admixture with chloride (Note 5).

Permanganic anhydride (violet vapour; explosive): from permanganate.

Notes. — 1. Some chlorides, notably HgCl, $HgCl_2$, AgCl, $SnCl_2$, and $PbCl_2$, do not yield HCl readily. In the case of HgCl and $SnCl_2$, SO_2 is formed by reduction of the H_2SO_4.

2. If much concentrated H_2SO_4 is used, bromide in small quantity may be overlooked, as the bromine dissolves in the excess of acid.

3. Carbon monoxide (from oxalate) is not easily identified in presence of other gases, *e.g.* CO_2 from carbonate.

4. In absence of sulphite and thiosulphate, evolution of SO_2 may indicate (*a*) reduction of the H_2SO_4 by a metal, a sulphide, sulphur, carbon (arising, *e.g.*, from charring of tartrate), etc.; (*b*) the presence of thiocyanate if the SO_2 (mixed with COS, CO_2, etc.) is accompanied by separation of sulphur.

5. Chromyl chloride is liable to be mistaken for bromine. It forms a greenish-yellow vapour (compare bromine) which condenses very readily, forming deep red liquid drops (B.P. 118°). Bromine is more volatile (B.P. 60°). Chromyl chloride interacts with water and fumes in moist air, forming H_2CrO_4 and HCl. The odour differs, therefore, from that of bromine.

The above preliminary and general examination for acidic radicals (8*a* and 8*b*) should be carried out very carefully. Although the results obtained are not invariably conclusive, they indicate what supplementary or confirmatory tests are necessary.

PREPARATION OF A SOLUTION OF THE SUBSTANCE.

The general appearance of the substance and the results obtained in the preliminary examination will often afford guidance as to the best procedure to be followed in preparing a solution for analysis. Some notes on specific cases are appended (p. 38).

If the substance is metallic, refer to p. 73; if it is a mineral, refer to p. 75.

I. Selection of a Solvent.

Try to dissolve a little of the substance in one of the following solvents, in the order named: (1) water, (2) dilute HCl, (3) concentrated HCl, (4) dilute HNO_3, (5) concentrated HNO_3, (6) aqua regia (3 c.c. concentrated HCl+1 c.c. concentrated HNO_3).

Procedure.—(1) In a test-tube mix about 0·05 gram of the substance with 5 c.c. of water and boil gently. If the substance is completely soluble, see II. (p. 38).

(2) If the substance is not completely soluble in water, mix a fresh portion with 5 c.c. of dilute HCl and boil gently. If the substance does not wholly dissolve, try the other solvents in the order named; use not more than 2 to 4 c.c. of concentrated acid. Concentrated HNO_3 and aqua regia should be avoided unless they appear to be more effective than HCl; concentrated HCl mixed with one-third of its volume of hydrogen peroxide is sometimes very efficient and avoids the introduction of nitrate.

(3) Sometimes all but a very small portion of the substance dissolves in a given solvent. In that case, decant the solution into another tube and ascertain whether the small residue will dissolve in a few drops of fresh acid solvent. If this is the case, add this portion to the main solution. If a very slight residue still remains, it may be a trace of silica or a silicate (especially if the substance is a mineral) and may be confirmed by means of a microcosmic bead test. (In the analysis of simple mixtures, a *minute*

residue is usually an accidental impurity and may be neglected.)

(4) A comparatively large residue left after boiling the substance with concentrated acid may dissolve in water. In this case, decant the liquid into another tube and ascertain whether the residue dissolves on adding water.

(5) The action of acids on the substance may lead to the formation of new insoluble substances not present in the original substance, *e.g.*, AgCl, $PbCl_2$, sulphur, sulphates, etc. The formation of such insoluble substances may sometimes be avoided by selecting another solvent; or sometimes by (*a*) extracting the substance with water, filtering, and washing the residue, (*b*) dissolving the residue in acid; these two solutions must then be examined separately.

(6) If the substance will not dissolve completely in any of these solvents, select the solvent that appears to be most effective and proceed as described below.

II. Preparation of the Solution.

Gently boil not more than 0·5 gram of the substance with the selected solvent. Not more than 10 c.c. of dilute acid or 5 c.c. of concentrated acid is usually required. If the substance has been dissolved in *concentrated* acid, dilute the solution with an equal volume of water; AgCl may be precipitated. (If much water is added, BiOCl or SbOCl may be precipitated.) Cool the solution under the tap; $PbCl_2$ may be precipitated in the form of white, needle-shaped crystals.

If the substance cannot be dissolved completely, filter (hot), and wash the insoluble residue with hot water. Cool the solution as described above and proceed with the analysis. The insoluble residue is examined separately (p. 68).

Notes.—1. Dilute HCl is frequently the best solvent for insoluble carbonates, oxalates, and phosphates, and for many oxides, sulphides, and basic salts. Concentrated HCl is necessary for some sulphides (*e.g.*, Sb_2S_3) and for some oxides (*e.g.*, Fe_2O_3) and dioxides (*e.g.*, PbO_2, MnO_2).

Dilute HNO_3 is useful for oxides, carbonates, etc., of the metallic radicals in Group I. ($Ag^{\cdot}$, $Hg^{\cdot}$, $Pb^{\cdot\cdot}$).

Concentrated HNO_3 is required for some sulphides (*e.g.*, CuS, FeS_2),

and aqua regia for HgS, SnS_2 (mosaic gold), etc. These solvents are avoided if possible.

2. If the substance (whether soluble in water or not) contains chromate or permanganate, it should be boiled with concentrated HCl so as to reduce these substances to chromic or manganous salts.

3. If the substance contains organic matter (oxalate, tartrate, etc.), it is sometimes advisable to destroy the latter at this stage:—Ignite the substance in a porcelain crucible at a low temperature until fully charred. After cooling, add a few drops of concentrated HNO_3 and ignite again. If any carbon remains, repeat the treatment with HNO_3 and the ignition. Note, however, that mercury and arsenic compounds may be volatilised during the ignition, and for this reason it may be advisable to postpone the elimination of organic matter until a later stage (p. 44).

4. Complex cyanogen radicals (ferrocyanide, etc.) should be decomposed before preparing the solution for analysis, in the following way:—In a porcelain crucible, mix about 0·5 gram of the substance with 1 c.c. of concentrated H_2SO_4 so as to form a thin paste. Place the crucible obliquely over a small flame and heat *gently* until fuming ceases. Cool. Warm the residue with concentrated HCl and dilute with water. Filter, if necessary. (An insoluble residue may be $BaSO_4$, $SrSO_4$, or $PbSO_4$.)

The solution will contain not only the metallic radicals present in the substance but also the metals (*e.g.*, Fe) present originally in the complex cyanogen radical.

SYSTEMATIC EXAMINATION FOR METALLIC RADICALS.

Outline of Separation into Groups.

(*Full details are given on pp.* 41-46.)

To the solution of the substance add dilute HCl in slight excess. Filter.

<table>
<tr>
<td rowspan="5">Precipitate.
AgCl
HgCl
$PbCl_2$
Group I.
Examine as described on p. 46.</td>
<td colspan="5">Filtrate :—Dilute with water. Saturate with H_2S. Filter.</td>
</tr>
<tr>
<td rowspan="4">Precipitate.
CuS, HgS, PbS, Bi_2S_3, CdS, As_2S_3, SnS, SnS_2, Sb_2S_3.
Group II.
Examine as described on p. 47.</td>
<td colspan="4">Filtrate :—Expel H_2S. Oxidise $Fe^{\cdot\cdot}$ salts. Eliminate silicate, fluoride, oxalate, tartrate, and phosphate. Add NH_4Cl and a slight excess of NH_4OH. Filter.</td>
</tr>
<tr>
<td rowspan="3">Precipitate.
$Fe(OH)_3$
$Al(OH)_3$
$Cr(OH)_3$
[MnO(OH)]
Group III.
Examine as described on p. 50.</td>
<td colspan="3">Filtrate :—Saturate with H_2S. Filter.</td>
</tr>
<tr>
<td rowspan="2">Precipitate.
ZnS
MnS
CoS
NiS
Group IV.
Examine as described on p. 51.</td>
<td colspan="2">Filtrate :—Expel excess of NH_4 salts. Add NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$. Filter.</td>
</tr>
<tr>
<td>Precipitate.
$CaCO_3$
$SrCO_3$
$BaCO_3$
Group V.
Examine as described on p 53.</td>
<td>Filtrate :—
Group VI.
Expel NH_4 salts, and examine the residue for $Mg^{\cdot\cdot}$, $Li^{\cdot}$, $Na^{\cdot}$, and $K^{\cdot}$, as described on p. 54.</td>
</tr>
</table>

Examine the original substance for $NH_4^{\cdot}$ as described on p. 56.

In this section (pp. 40-56) the arrangement is as follows :—

1. Separation into Groups (pp. 40-46).

The tabular outline given above shows how (without going into details) each group is precipitated and separated by filtration—the filtrate in each case being examined for

the group that immediately follows. The method of precipitation of each group is then described in detail.

2. Analysis of the Groups (pp. 46-56).

For each group there is given (1) a tabular outline of the method of analysis, (2) " Procedure " in which the method of analysis is described in detail.

SEPARATION INTO GROUPS.

(*See Outline on p.* 40.)

Group I.

To the solution of the substance, prepared as directed on p. 37, add a few drops of dilute HCl (unless HCl was used in preparing the solution); if a precipitate forms, add more acid slowly, until after warming, vigorously shaking and allowing the precipitate to settle, no further precipitate is seen to form when another drop of acid is added to the clear liquid. Then add an excess of 3 to 4 drops of acid, cool thoroughly under the tap, and filter. Examine the precipitate for the radicals of Group I. as described on p. 46. (The filtrate is examined for Group II. and following groups.)

Notes.—1. A large excess of HCl must be avoided. The chlorides of $Ag^{\cdot}$, $Hg^{\cdot}$, and $Pb^{\cdot\cdot}$ are less soluble in very dilute HCl than in water, but are more readily soluble in concentrated HCl, owing to the formation of complex ions.

2. If the substance was completely soluble in dilute HCl, or if the addition of dilute HCl produces no precipitate, neither $Ag^{\cdot}$ nor $Hg^{\cdot}$ is present. When $Pb^{\cdot\cdot}$ is present, $PbCl_2$ may not be precipitated unless the hot solution is thoroughly cooled. If only a small quantity of $Pb^{\cdot\cdot}$ is present, it may not be precipitated in Group I. (see Note 1, p. 7).

3. If the substance was dissolved in dilute HNO_3, HCl may precipitate BiOCl or SbOCl, but these dissolve readily in excess of acid.

4. If the solution is originally alkaline, the addition of dilute HCl (or HNO_3) may precipitate certain substances other than insoluble chlorides, *e.g.*—

sulphur, from polysulphide or thiosulphate ;
As_2S_3, Sb_2S_3, SnS_2, from a solution containing thiosalts ;
silicic acid from an alkali silicate ;
an insoluble cyanide from a solution containing a complex cyanide, such as $KAg(CN)_2$.

With the exception of AgCN, these substances are not likely to be mistaken for a chloride of $Ag^{\cdot}$, $Hg^{\cdot}$, or $Pb^{\cdot\cdot}$ (it is sufficient to note that they are precipitated by HNO_3). The colour, or the information from the preliminary examination, will usually suggest how such a precipitate should be examined.

Group II.

If the substance was dissolved in HNO_3, or in aqua regia, evaporate the solution (or the filtrate from Group I) almost to dryness, add 5 c.c. of dilute HCl, and dilute wit a little water.

Transfer the solution to a small flask (150 c.c.) and dilute with warm water to about 40 c.c. (Note 1). Saturate with H_2S as described on p. 5. If a precipitate is obtained, warm, and filter: wash the precipitate with 10 c.c. of H_2S solution, and add the washings to the filtrate. Test the filtrate with methyl violet and, if necessary, dilute with water so as to make the concentration of acid about 0·3N (Note 2). Saturate again with H_2S. If more precipitate forms, warm, and filter through the original filter. Wash the precipitate with hot water containing H_2S, and examine it for the Copper and Arsenic Groups as described on p. 47.

If arsenic may possibly be present as arsen*ate*, add to the filtrate about 5 c.c. of concentrated HCl and 2 c.c. of 10 per cent. NH_4I solution, heat until boiling, and again saturate with H_2S (Note 3). If As_2S_3 (mixed with sulphur) is precipitated, boil, and filter through a new paper. Finally, make certain that the precipitation of As_2S_3 is complete by boiling again and saturating with H_2S once more. Wash the precipitate and examine it for As_2S_3 only.

Examine the filtrate for Group III., as indicated on p. 43.

Notes.—1. Dilution with water may cause precipitation of BiOCl or SbOCl. These basic salts must not be filtered, or redissolved by the addition of more HCl; they are readily converted into less soluble sulphides by H_2S.

2. The solution must contain sufficient HCl to prevent the precipitation of zinc, cobalt, and nickel sulphides, but the concentration of HCl must not exceed about 0·3N, otherwise the precipitation of lead and cadmium sulphides will be incomplete or may be altogether prevented. (Concentrated HCl is about 10N, and the dilute acid about 2N ; therefore 5 c.c. of the dilute acid must be diluted to about 35 c.c. to make the concentration 0·3N). Methyl violet may be used as an

indicator in order to ascertain whether the concentration of acid has been adjusted properly. The solution should give a blue-green or a blue colour when 2 drops are mixed with a minute drop of methyl violet solution on a white porcelain surface. If the colour is yellow-green or yellow, the solution is too acid.

3. Arsenic, when present as arsen*ate* with dilute HCl (arsen*ic* acid), is precipitated by H_2S exceedingly slowly in the cold. If the solution is heated to its boiling-point, the precipitation takes place more readily although not rapidly; the arsen*ic* acid is reduced to arsenious acid and the arsenic precipitated as As_2S_3, mixed with sulphur. Care must be taken, on this account, that As, in the form of arsenate, is not overlooked.

Arsen*ic* acid is readily reduced by means of hydriodic acid (or ammonium iodide in presence of hydrochloric acid), and precipitation with H_2S then takes place rapidly.

$$As_2O_5 + 4HI \rightleftharpoons As_2O_3 + 2H_2O + 4I$$
$$\downarrow 3H_2S \qquad\qquad \downarrow 2H_2S$$
$$As_2S_3 + 3H_2O \qquad 4HI + 2S.$$

4. If the solution contains an oxidising agent, such as nitric acid, a bichromate, a permanganate, or a ferric salt, the H_2S is oxidised and sulphur (white) is precipitated. If a bichromate is present, the colour of the solution changes from orange-red to green; if a permanganate or a ferric salt is present, the solution becomes colourless. It is preferable, however, to reduce chromates, bichromates, and permanganates by boiling the original substance with a little concentrated HCl when preparing the solution for analysis. If nitric acid is present, it is removed for the most part as indicated above.

5. Colours of the sulphides:—

Black: HgS, CuS, PbS.
Dark brown: Bi_2S_3, SnS.
Yellow: CdS, As_2S_3, As_2S_5, SnS_2.
Orange: Sb_2S_3, Sb_2S_5.

Mercuric salts give at first a white precipitate ($HgCl_2$, 2HgS) which with more H_2S becomes yellow, brown, and finally black (HgS). If much HCl is present, lead salts may give a red precipitate ($PbCl_2$, 2PbS) which becomes black (PbS) with excess of H_2S or on dilution.

Group III.

Preliminary Treatment of the Filtrate from Group II.—Before attempting the precipitation of the Iron Group, the filtrate from Group II. must receive the following treatment:—

(1) H_2S must be removed by boiling.

(2) Ferrous salts must be oxidised and converted into ferric salts.

(3) Silicate, fluoride, oxalate, tartrate, and phosphate must be eliminated; silicate, by evaporating the solution to dryness; fluoride, by repeated evaporation with concentrated HCl; organic radicals, by evaporation to dryness and gentle ignition; phosphate, as indicated below.

Boil the filtrate in a basin for about five minutes and evaporate, if necessary, to about 10 c.c. If ferrous salt is present [test a few drops with $K_3Fe(CN)_6$], add about 10 drops of concentrated HNO_3 and boil again for a few moments.[1]

If silicate, fluoride, oxalate, or tartrate is present (Note 1) add 10 c.c. of concentrated HCl, evaporate to dryness and repeat the evaporation with HCl once more (Note 2); then (only if organic radicals are present) place the basin on a pipe-clay triangle and heat the residue to a moderately high temperature (not to visible redness) in order to destroy organic matter. When the basin is cold, add 2 c.c. of concentrated HCl, warm gently, add 10 c.c. of water, warm again, and then filter, if necessary, from insoluble silica or carbon.

To 1 c.c. of the solution, add 1 c.c. of NH_4Cl, NH_4OH until alkaline, and boil. If a precipitate is obtained, note its colour, then redissolve it in a few drops of concentrated HNO_3 and test the solution for phosphate[2] by adding an equal volume of ammonium molybdate solution and warming. If a precipitate is obtained with NH_4Cl and NH_4OH, phosphate, if present, must be eliminated as follows:—

To the main portion of the solution add 10 c.c. of concentrated HNO_3, evaporate to dryness and repeat the evaporation with HNO_3 once more. Then add 8 c.c. of concentrated HNO_3 and about 1 gram of pure granulated tin. Boil gently and evaporate to a small volume. Dilute with about 20 c.c. of water and, if time permits, set aside for

[1] If iodine is liberated here, add more HNO_3 and volatilise the iodine by boiling.

[2] Test for PO_4''' here, whether a precipitate was obtained with NH_4OH or not.

an hour. Filter. (Reject the precipitate.) The filtrate is now free from PO_4''' (Note 3).

Precipitation of the Group.—To the filtrate from Group II. (after the above preliminary treatment, so far as was necessary) add 2 grams of solid NH_4Cl, heat until boiling, and then add NH_4OH carefully until, after thorough shaking, the mixture smells of NH_3. Boil again for a moment (make certain that NH_3 is present in the escaping steam) and filter. Examine the precipitate as described on p. 50.

Notes.—1. These radicals, with the possible exception of oxalate, are readily detected in the preliminary examination. Unless oxalate has been previously eliminated (Note 3, p. 39) or proved absent, its possible presence here should be considered.

Silicate is commonly met with only in minerals and metallurgical products.

2. In the absence of fluoride, only one evaporation (without the addition of concentrated HCl) is necessary. Fluoride is more readily eliminated by evaporation with concentrated H_2SO_4, but a white residue insoluble in water must not be overlooked and should be examined for $BaSO_4$ or $SrSO_4$.

3. If no precipitate is obtained with NH_4Cl and NH_4OH *in presence of* PO_4''', the absence of not only $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, but also of $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, and $Mg^{\cdot\cdot}$ is indicated. In that case, PO_4''' need not be eliminated, and only the Zinc Group, $Li^{\cdot}$, $Na^{\cdot}$, and $K^{\cdot}$ need be looked for.

Group IV.

Evaporate the filtrate from the Iron Group, if necessary, until the volume is reduced to about 25 c.c. Add NH_4OH until it is decidedly alkaline. To a small portion add H_2S solution and warm gently. If a precipitate is obtained, place the whole solution in a small flask, heat until almost boiling, and saturate with H_2S as described on p. 5. Filter, and wash the precipitate at once with hot NH_4Cl solution containing a little H_2S.

Examine the precipitate as described on p. 51.

Notes.—1. Ammonium sulphide (freshly prepared) may be used to precipitate this Group instead of saturating the alkaline solution with H_2S. A large excess of ammonium sulphide must be avoided.

2. NiS dissolves somewhat readily in yellow ammonium sulphide forming, probably, a colloidal solution, and giving rise to a dark-brown filtrate. If the filtrate is brown, acidify it with acetic acid, boil for a few moments, and collect the NiS precipitate on a new filter.

Group V.

Evaporate the filtrate from the Zinc Group to complete dryness. Place the basin (a small one) on a pipe-clay triangle and ignite gently until most of the ammonium salts are expelled. Dissolve the residue in a few drops of HCl and 10 c.c. of water, and filter from any carbonaceous matter.

To the filtrate add 5 c.c. of NH_4Cl, 5 c.c. of NH_4OH, and 5 to 10 c.c. of $(NH_4)_2CO_3$. Keep near the boiling-point for about a minute, and filter. Examine the precipitate as described on p. 53.

Notes.—1. The carbonates of calcium, strontium, and barium are quite appreciably soluble in concentrated NH_4Cl solution. Sufficient NH_4Cl must be present, however, in order to prevent precipitation of magnesium carbonate.

2. The solution is warmed (but not boiled) in order to decompose bicarbonates and carbamates which are soluble; at the same time the precipitate, originally voluminous and flocculent, becomes crystalline.

Group VI.

The filtrate from the Calcium Group is examined for $Mg^{\cdot\cdot}$, $Li^{\cdot}$, $Na^{\cdot}$, and $K^{\cdot}$, as described on p. 54. The original substance is examined for $NH_4^{\cdot}$.

ANALYSIS OF THE GROUPS.

In the brief tabular outline given for each Group, the numbers refer to the correspondingly numbered paragraphs in the detailed procedure that follows.

Analysis of Group I.

Outline.

Precipitate (1): AgCl, HgCl, $PbCl_2$. Wash with cold water. Boil with water. Filter.

<table>
<tr><td colspan="2">Residue (3): AgCl, HgCl. Wash with hot water. Pour NH_4OH through the filter.</td><td rowspan="2">Filtrate (2): — Add K_2CrO_4: yellow precipitate shows Pb.</td></tr>
<tr><td>Residue (5): — If black, is $Hg(NH_2)Cl+Hg$, and shows Hg.</td><td>Filtrate (4):—Add HNO_3: white precipitate shows Ag.</td></tr>
</table>

Procedure.

(1) Wash the precipitate three times with a little cold water by blowing a fine stream from the wash-bottle round the upper edge of the filter and allowing each portion (5 c.c.) to drain before adding the next. The first portion of the washings should be added to the original filtrate which is to be examined for Group II., etc. Pierce the apex of the filter paper with a pointed glass rod, wash the precipitate into a test-tube with 15 to 20 c.c. of water, boil the mixture, and filter.

(2) Test a portion of the filtrate (2) for Pb with K_2CrO_4.

(3) If Pb is present, wash the residue (3) with hot water (from a wash-bottle) until 5 c.c. of the washings give no precipitate with K_2CrO_4. Then pour 10 c.c. (in all) of NH_4OH several times through the filter.

(4) Acidify the filtrate (4) with HNO_3: a white, curdy precipitate shows the presence of Ag.

(5) A black residue (5) on the filter shows the presence of Hg, which may be readily confirmed by a dry-way test.

Analysis of Group II.

Separation of the Copper and Arsenic Groups.

Wash the sulphide precipitate with hot water containing a little H_2S. Warm a small portion of the precipitate with about 2 c.c. of NaOH and 5 drops of yellow ammonium sulphide (Note 1); filter, and add HCl to the filtrate until it is acid. If no precipitate (except white sulphur) forms, examine the main sulphide precipitate for the Copper Group only (the Arsenic Group being absent). If a precipitate (not being white sulphur) forms, warm the main sulphide precipitate in a porcelain basin with about 20 c.c. of NaOH and 5 c.c. of yellow ammonium sulphide (Note 1). Filter.

Residue.—Examine for the radicals of the Copper Group as described on p. 48.

Filtrate.—Examine for the radicals of the Arsenic Group as described on p. 49.

Note 1.—Yellow ammonium sulphide [ammonium polysulphide, $(NH_4)_2S_x$] is required only if SnS is present and should otherwise be omitted, since CuS is somewhat soluble in yellow ammonium sulphide and HgS in sodium sulphide (or a mixture of NaOH and yellow ammonium sulphide).

ANALYSIS OF COPPER GROUP.

Outline.

Precipitate (1): CuS, HgS, Bi_2S_3, PbS, CdS. Wash with hot water containing H_2S. Boil with 3·3N HCl. Filter.

<table>
<tr><td rowspan="3">Residue (2):
CuS, HgS.
Dissolve in $HCl+HNO_3$, dilute the solution and test portions for –
(*a*) Cu by adding $K_4Fe(CN)_6$.
(*b*) Hg by adding $SnCl_2$.</td><td colspan="3">Filtrate (3) :—Add NH_4OH in excess Filter.</td></tr>
<tr><td colspan="2">Precipitate (4): $Pb(OH)_2$, $Bi(OH)_3$. Dissolve in HCl, add K_2CrO_4 and excess of NaOH. Filter.</td><td rowspan="2">Filtrate (7) :—
If blue, add KCN until colourless. Then add H_2S : yellow pp. shows Cd.</td></tr>
<tr><td>Precipitate (5):
$(BiO)_2Cr_2O_7$.
Dissolve in HCl and add to sodium stannite: black pp. shows Bi.</td><td>Filtrate (6) :—
Acidify with acetic acid: yellow pp. shows Pb.</td></tr>
</table>

Procedure.

(1) Wash the precipitate with hot water containing H_2S. Transfer it to a porcelain basin. Add 10 c.c. of water and 5 c.c. of concentrated HCl. Boil gently for about a minute. Filter. Examine the filtrate by (3).

(2) Wash the residue with hot water. Transfer to a porcelain basin. Add 3 c.c. of concentrated HCl and 3-4 drops of concentrated HNO_3. Boil gently and evaporate almost to dryness. Dilute with a little water, and filter. Divide into two portions:—

(*a*) Add NH_4OH until alkaline, acidify with acetic acid, and add a drop of $K_4Fe(CN)_6$: a brown precipitate shows Cu.

(*b*) Add $SnCl_2$: a white precipitate, which becomes grey with excess of $SnCl_2$, shows Hg.

(3) Expel H_2S and evaporate the filtrate (3) to about 5 c.c. Add NH_4OH in distinct excess. Boil, and filter. Examine the filtrate by (7).

(4) Wash the precipitate with hot water. Dissolve in a very little warm, dilute HCl, add K_2CrO_4 and excess of NaOH. Filter. Examine the filtrate by (6).

(5) Wash the precipitate. Pour about 1 c.c. of dilute

HCl over it and allow to drop into freshly prepared sodium stannite: a black precipitate confirms Bi. [Sodium stannite is prepared by taking a few drops of $SnCl_2$ solution, diluting to 5 c.c. and adding NaOH, drop by drop, until the precipitated $Sn(OH)_2$ redissolves].

(6) Acidify the filtrate (6) with acetic acid: a yellow precipitate shows Pb.

(7) If the filtrate (7) is blue, add KCN until it is colourless (in any case add a few drops of KCN), and then pass H_2S for a few seconds: a yellow precipitate shows Cd.

Analysis of Arsenic Group.

Outline.

To the solution (obtained by warming the H_2S precipitate with NaOH and yellow ammonium sulphide, and then filtering), add Na_2O_2, boil, and filter (1).

<table>
<tr><td rowspan="3">Precipitate (2): HgS. Confirm by dissolving in $HCl+HNO_3$, and adding $SnCl_2$: a white or grey precipitate shows Hg.</td><td colspan="3">Filtrate (3):—Add solid NH_4Cl, boil, and filter.</td></tr>
<tr><td rowspan="2">Precipitate (4): $Sn(OH)_4$. Dissolve in HCl. Warm the solution with Fe. Cool, and filter into $HgCl_2$: a white or grey precipitate shows Sn.</td><td colspan="2">Filtrate (5):—Acidify with HCl, cool, and saturate with H_2S. Filter.</td></tr>
<tr><td>Precipitate (6):—Wash with hot water. Dissolve in concentrated HCl; filter if necessary, dilute, and pass H_2S: orange precipitate shows Sb.</td><td>Filtrate (7):—Add excess of HCl, and NH_4I. Boil, and saturate with H_2S: yellow precipitate shows As.</td></tr>
</table>

Procedure.

(1) While stirring the cold solution, which may contain As, Sb, Sn, and possibly Hg (as thio salts), add from 1·5 to 2 grams of sodium peroxide in small portions. Boil gently in a basin for three to four minutes. If a black precipitate separates, filter. Examine the filtrate by (3).

(2) If HgS is present in the H_2S precipitate, some of it may pass into the Arsenic Group and be found here. A black precipitate is examined as indicated in the outline.

(3) To the filtrate (3) add 3 to 4 grams of solid NH_4Cl, boil, and filter. Examine the filtrate by (5).

(4) Dissolve the precipitate by pouring 3 to 4 c.c. of hot concentrated HCl over it. Dilute the solution with an equal volume of water, add a clean iron nail (or fine iron wire, or levigated iron), and keep near the boiling-point for about a minute. Set aside for a few minutes. Cool, and filter (or decant) into a little $HgCl_2$: a white precipitate (which may become grey) shows Sn.

(5) Add HCl to the filtrate until it is *slightly* acid. Cool, and saturate with H_2S. Filter. Examine the filtrate by (7).

(6) The precipitate (6) is Sb_2S_5, but may contain a little As_2S_3. To confirm Sb:—Wash with hot water; warm with concentrated HCl, and filter from undissolved As_2S_3 if necessary; dilute with water, and pass H_2S: an orange precipitate shows Sb.

(7) Add to the filtrate (7) 5 c.c. of concentrated HCl, and 1 c.c. of NH_4I solution. Boil, and saturate with H_2S: a yellow precipitate (mixed with sulphur) shows As.

Analysis of Group III.

Outline.

Precipitate (1): $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, [MnO(OH)]. Wash with hot water. Mix with water, add Na_2O_2, and boil. Filter.

Residue (2): $Fe(OH)_3$, [MnO(OH)].	Filtrate (3): $NaAlO_2$, Na_2CrO_4.
Wash. Examine separate portions for Fe and Mn as indicated below.	Examine separate portions for Al and Cr as indicated below.

Procedure.

1. Wash the precipitate with hot water. Transfer it to a porcelain basin together with about 20 c.c. of water. Add about 1 gram of Na_2O_2, in small portions. Boil gently for 3 to 4 minutes. Dilute with a little water, and filter. Examine the filtrate according to (3).

2. Wash the residue with hot water. Test separate portions as follows:—

(*a*) Dissolve a portion in about 1 c.c. of concentrated HCl, dilute with water, and add KCNS: a deep-red coloration shows Fe; a faint-red coloration shows a trace of Fe. Ascertain by special tests whether the original substance contains a ferrous or a ferric compound or both:—Boil substance with HCl, filter if necessary, and test separate portions of the solution with $K_3Fe(CN)_6$ and KCNS.

(*b*) Boil a portion of the residue with dilute HNO_3 and about 1 gram of PbO_2 (free from Mn). Allow the PbO_2 to settle and examine the clear liquid: a pink or violet-red coloration indicates Mn. Or, examine a portion of the residue for Mn by the sodium carbonate bead test (p. 30).

With regard to the partial precipitation of Mn in the Iron Group, see Note 2 on p. 7.

3. If the filtrate (3) is yellow, Cr is present. Confirm by acidifying a portion of the filtrate with acetic acid and adding lead acetate: a yellow precipitate shows Cr. Ascertain by special tests whether the Cr is present in the original substance as a chromic salt or a chromate, or as both.

To another portion of the filtrate (3) add about 1 c.c. of clear litmus solution (sufficient to colour the solution distinctly blue), then add excess of solid NH_4Cl, and boil. Set aside for a few minutes and then examine: a flocculent precipitate, stained blue by the litmus, shows Al.

Analysis of Group IV.

Outline.

Precipitate (1): ZnS, MnS, CoS, NiS. Wash the precipitate. Mix it with cold, dilute HCl. Filter.

<table>
<tr><td rowspan="2">Residue (2):
CoS, NiS. Test for Co and Ni by borax bead, and as indicated below.</td><td colspan="2">Filtrate (3):—Expel H_2S. Cool, and add excess of NaOH. Filter (cold).</td></tr>
<tr><td>Precipitate:
$Mn(OH)_2$, [$Ni(OH)_2$]. Confirm Mn by sodium carbonate bead test.</td><td>Filtrate (4):—
Acidify with acetic acid, and add H_2S. Confirm Zn by Rinnmann's green test.</td></tr>
</table>

Procedure.

(1) Wash the precipitate, preferably with warm NH_4Cl solution containing a little H_2S. If the precipitate is black (Ni or Co present, or possibly both), transfer it to a basin, add 20 c.c. of water, and then 5 c.c. of dilute HCl. Stir for a few minutes, and filter. If the precipitate is not black, dissolve it in hot dilute HCl by pouring the acid into the filter. Examine the filtrate by (3).

(2) Wash the black residue (2) with hot water. Examine a portion in a borax bead.

A blue bead shows Co. The precipitate must be examined further for Ni (but see Note 2 on p. 45).

A distinct reddish-brown bead shows Ni. The precipitate *may* be examined further for a trace of Co.

An uncertain brownish-bead shows the probable presence of both Ni and Co — the latter in comparatively small quantity. The precipitate *must* be examined further for both Ni and Co.

The procedure is as follows:—Transfer the precipitate to a basin and dissolve it in the smallest possible quantity of concentrated HCl with 2 to 3 drops of concentrated HNO_3. (If the precipitate is very small, incinerate the filter paper together with the precipitate in a porcelain crucible and dissolve the ash as above.) Evaporate until just dry. (A blue residue shows Co; a yellow residue shows Ni only.) Dissolve in 10 c.c. of water, and filter (sulphur) if necessary. If both Ni and Co have to be tested for, divide the solution into two portions.

Ni test.[1] Add KCN solution, drop by drop, until the precipitate which forms just redissolves (avoid large excess). Boil the solution in a basin for a minute. Add 5 c.c. of NaOH and 10 c.c. of Br-water, and warm: a black precipitate shows Ni. Filter, wash, and confirm by borax bead.

Co test. Add acetic acid and then an equal volume of concentrated KNO_2 solution: a yellow precipitate, which may appear only after some hours, shows Co.

[1] Alternative test for Ni:—Add diacetyldioxime (1 per cent. solution in alcohol) and a few drops of NH_4OH, and warm: a red, flocculent precipitate shows Ni.

(3) Boil the filtrate (3) in a basin in order to expel H_2S completely. Add a few drops of concentrated HNO_3, boil again, and evaporate to 10 c.c. Filter if the solution is not clear, and cool. Add NaOH until decidedly alkaline, and filter (cold). Confirm Mn in the precipitate by the sodium carbonate bead test. [A small, pale-green precipitate is probably $Ni(OH)_2$: confirm by borax bead.]

(4) Acidify the filtrate (4) with acetic acid and add H_2S: a white precipitate, which is sometimes discoloured owing to traces of other sulphides, such as PbS, shows Zn. To confirm Zn:—Filter, dissolve the precipitate in a few drops of HNO_3, and add 1 drop of $Co(NO_3)_2$. Fold up a small filter paper, wrap a platinum wire round it, and soak the paper in the solution. Ignite the paper in the oxidising flame: a green residue shows Zn.

Analysis of Group V.

Outline.

Precipitate (1): $CaCO_3$, $SrCO_3$, $BaCO_3$. Wash with hot water. Dissolve in hot acetic acid. Add K_2CrO_4 in slight excess. Warm, and filter.

<table>
<tr><td rowspan="2">Precipitate (2): $BaCrO_4$.
Wash. Confirm Ba by flame test.</td><td colspan="2">Filtrate (3):—Add excess of $(NH_4)_2CO_3$. Warm and filter.</td></tr>
<tr><td>Precipitate (4): $CaCO_3$, $SrCO_3$.
Wash. Dissolve in hot acetic acid. Make the solution alkaline with NH_4OH. Test separate portions for Ca and Sr as indicated below.</td><td>Filtrate:—Neglect.</td></tr>
</table>

Procedure.

1. Wash the precipitate with hot water. Dissolve it in hot acetic acid, using as little as possible. (Pour the acid, drop by drop, into the filter, and return the filtrate once or twice to the filter until complete solution has been effected; 3 to 4 c.c. of acid ought to suffice.) Neutralise the solution with NH_4OH, and then add 2 c.c. of acetic acid.

To 1 c.c. of this solution, add an equal volume of water

and a few drops of K_2CrO_4. If there is no precipitate (Ba absent), examine the main portion of the solution for Ca and Sr as indicated in (4). If Ba is present, dilute the main portion of the solution to about 15 c.c., heat until boiling, and add hot K_2CrO_4 solution until precipitation is complete. Keep near the boiling-point for about a minute, and filter. Examine the filtrate by (3).

2. Wash the precipitate (2) with hot water. Moisten a portion of it on a watch-glass with a drop of concentrated HCl, and confirm Ba by the flame coloration.

3. The filtrate (3) must be orange in colour. Heat until boiling, and add $(NH_4)_2CO_3$ until the orange-coloured solution becomes yellow, then add an additional 2 to 3 c.c. Keep near the boiling-point for about a minute, and filter. Neglect the filtrate.

4. Wash the precipitate (4). Dissolve a small portion in 1 drop of HCl, and examine the flame coloration with the aid of the spectroscope (p. 28). Dissolve the main portion in acetic acid, and make the solution alkaline with NH_4OH. (The volume of the solution should not be more than 5 c.c.) Divide the solution into two portions.

(*a*) Add an equal volume of $CaSO_4$ solution and boil: a white precipitate or turbidity indicates Sr. Filter, wash, and confirm by flame coloration.

(*b*) Make certain that the solution is alkaline. Add about 1 gram of solid NH_4Cl and an equal volume of saturated $K_4Fe(CN)_6$ solution, and warm *very gently:* a fine, white precipitate indicates Ca.

Analysis of Group VI.

Outline.

Filtrate from Group V.:—Remove traces of Group V. Evaporate to dryness. Expel NH_4 salts. Dissolve residue in dilute HCl, and filter. Divide the filtrate into two portions. Examine one portion for Mg and the other for Li, Na, and K, as indicated below.

Test the original substance for NH_4.

Procedure.

Evaporate the filtrate from Group V. until its volume is about 10 c.c. In order to precipitate any traces of calcium, strontium, and barium, add about 1 c.c. of $(NH_4)_2C_2O_4$, 2 to 3 drops of dilute H_2SO_4, and 5 c.c. of NH_4OH. Heat until boiling, and filter. (Reject any precipitate.)

Evaporate the filtrate to dryness in a small basin. Place the basin on a pipe-clay triangle and ignite gently until all NH_4 salts are expelled. (Take care to heat the side as well as the bottom of the basin.) Allow the basin to cool. Dissolve the residue in 1 c.c. of dilute HCl, and add 5 c.c. of water. Filter through a small paper. (A little carbonaceous matter is usually present, arising from pyridine bases in the ammonia.) Divide the filtrate into two portions.

(1) *Magnesium.* Add 2 drops of $(NH_4)_2HPO_4$ and 5 c.c. of NH_4OH. If no precipitate appears immediately, shake vigorously for several minutes and set aside for ten minutes or longer. If a decided crystalline precipitate or turbidity is produced, Mg is present. If the solution remains perfectly clear, it may be set aside for 12 hours and again examined. Tiny crystals adhering to the glass—more easily seen if the liquid is poured away—indicate a trace of Mg.

Note.—As all phosphates, except those of Na, K, and NH_4, are insoluble in water (lithium phosphate is sparingly soluble), the above test for Mg is of no value unless all basic radicals other than Na, K, NH_4, and Mg have been removed completely in the earlier Groups. If Mn has been found, a trace is liable to escape prior precipitation, and as Mn forms crystalline $MnNH_4PO_4$ it may be mistaken for Mg.

A non-crystalline precipitate may be due, wholly or in part, to $AlPO_4$. It should be collected on a small filter, and a few drops of warm acetic acid poured over it. ($MgNH_4PO_4$ is soluble and $AlPO_4$ insoluble in acetic acid.) The solution is made decidedly alkaline with NH_4OH and shaken vigorously for several minutes, when a crystalline precipitate may now be obtained.

(2) *Sodium, potassium, and lithium.* Examine the flame coloration. A trace of Na will invariably be detected. Observe carefully, therefore, whether the yellow flame due to Na is feeble and fleeting or bright and persistent. Use a clean platinum wire and hold it near the base of the Bunsen flame.

Examine the flame coloration through deep cobalt-blue glass, and with the aid of the spectroscope. The lithium spectrum is highly characteristic (p. 28). Confirm the presence of potassium as follows:—Concentrate the solution by careful evaporation to 0·5 c.c. or less. Mix 1 drop each of $Na_2S_2O_3$ and $Bi(NO_3)_3$ solutions with 10 c.c. of alcohol. Add 1 to 3 drops of the solution to be tested: a yellow precipitate, easily soluble on addition of water, shows potassium.

Test for NH_4. Mix a small portion of the original substance in a small beaker with a gram of slaked lime and moisten with a little water. Cover the beaker with a watch-glass on the under side of which a piece of moist red litmus paper is made to adhere, and warm very gently. If NH_3 is evolved, it is usually easy to identify it by smell unless the quantity is very minute.

Lithium phosphate, on account of its slight solubility, may be precipitated by $(NH_4)_2HPO_4$ and mistaken for $MgNH_4PO_4$. In presence of much lithium, the following method of analysis may be used for Group VI.:—

To the solution, after removal of NH_4 salts, add $Ba(OH)_2$ solution in moderate excess, boil in a porcelain basin, and filter.

Precipitate.—This may contain $Mg(OH)_2$, $BaCO_3$, and possibly $BaSO_4$. Wash, and pour a small quantity of warm, dilute HCl over it. To the solution add dilute H_2SO_4, boil, and filter. Evaporate the filtrate to a small volume, and test for Mg by adding NH_4OH and $(NH_4)_2HPO_4$.

Filtrate.—Remove Ba by precipitation as $BaSO_4$, and test for Li, Na, and K as described above.

EXAMINATION FOR ACIDIC RADICALS.

The examination for acidic radicals consists of the following :—

I. Preliminary examination.
II. Evidence obtained in the course of the examination for metallic radicals.
III. Special tests.

I. PRELIMINARY EXAMINATION.

This is part of the general preliminary examination, and is carried out before the systematic examination for metallic radicals. It includes the following :—

(1) Sublimation tube test. See p. 22.
(2) Interaction of substance with dilute H_2SO_4. See p. 34.
(3) Interaction of substance with concentrated H_2SO_4. See p. 35.

II. EVIDENCE OBTAINED IN THE COURSE OF THE EXAMINATION FOR METALLIC RADICALS.

(1) **Arsenite and Arsenate.**—Neither of these radicals can be present unless As was found in Group II. If the precipitation of the As_2S_3 in Group II. was only completed by *boiling* the solution with H_2S, or after the addition of NH_4I, arsen*ate* is present (see Note 3, p. 43). It should be noted, however, that arsenate may have been formed by oxidation of arsenite if the substance was dissolved in HNO_3 or aqua regia.

(2) **Phosphate.**—This radical is tested for in the filtrate after removal of Group II. (see p. 44).

(3) **Chromate and Permanganate.**—The colour of the original substance or solution will usually afford evidence of the presence of these radicals. They are reduced to chromic and manganous salts in Group II. by H_2S, accompanied by corresponding colour changes. (See Note 4, p. 43.)

If chromate or permanganate is present, Cr and Mn will be found in Groups III. and IV. respectively, and special tests will be necessary to ascertain whether the substance contains chromic and manganous salts also.

(4) When the metallic radicals in a substance are known, the presence of certain acidic radicals is often excluded, according as the substance is soluble or not in water or in dilute acid.

Examples:—

(*a*) If the substance is soluble in water and Ba is present, it is needless to look for carbonate, sulphite, sulphate, chromate, phosphate, arsenate, borate, silicate, oxalate, etc. *Only acidic radicals that form soluble Ba salts can* be present.

(*b*) If the substance is insoluble in water, but soluble in dilute acid, and Ag and Ba are present, it is unnecessary to test for chloride, bromide, iodide, cyanide, ferrocyanide ferricyanide, thiocyanate, and sulphate.

III. SPECIAL TESTS.

Before proceeding to make special tests for individual acidic radicals, it is expedient to review the results obtained in the general and preliminary examination, and in the examination for metallic radicals, in order to see how far these results anticipate or narrow down the problem.

Such a review will probably show—

(*a*) That certain acidic radicals have been already definitely proved present or absent, *e.g.* CO_3'', S'', NO_2', PO_4''', AsO_4''', MnO_4', etc.

(*b*) That certain acidic radicals are, in some cases, necessarily absent, *e.g.* SO_4'', if Ba is present and the substance is soluble in dilute acid.

(*c*) That supplementary tests for certain acidic radicals are necessary, *e.g.* for Cl', Br', I', NO_3', etc.

(*d*) That no tests have yet been made for certain acidic radicals, *e.g.* SO_4'' and BO_3'''.

Preparation of a Solution for the Special Tests.

The metallic radicals (except Na, K, and NH_4) present in the substance may interfere with the special tests for acidic radicals, and it is advisable, as a general rule, to prepare a solution for these tests which contains the acidic radicals as alkali salts. Two cases may be distinguished:—

(1) **The Substance contains only Na, K, and NH_4 Salts.**—In this case dissolve about 0·25 gram of the substance in about 20 c.c. of water, and use this solution for the special tests as indicated below. If this solution is alkaline, salts of weak acids, such as carbonate, sulphite, acetate, borate, phosphate, are probably present; if it is acid, the probable presence of acid salts, or ammonium salts of strong acids, is indicated.

(2) **The Substance contains other Metallic Radicals.**—In this case mix about 0·25 gram of the substance with about 1 gram of sodium carbonate (anhydrous) and 25 c.c. of water. Boil the mixture for several minutes in a basin or small flask, and filter. The "sodium carbonate extract" contains the acidic radicals, together with an excess of sodium carbonate, and is used as indicated below for the special tests.

Notes.—1. Many salts are not decomposed or are very imperfectly decomposed by boiling with sodium carbonate, *e.g.* many sulphides and silicates; phosphates and fluorides of calcium and barium; aluminium phosphate; but the acidic radicals in such cases can usually be identified in other ways. *Fusing* with sodium carbonate is more efficient and is sometimes necessary, as with silicate minerals and glasses; the fused mass (on platinum foil) is boiled with water and filtered, and the filtrate is used for the tests.

Arsenic is not precipitated by sodium carbonate, and in other cases precipitation of the metallic radical is incomplete on account of complex ion formation, *e.g.* copper in presence of an ammonium salt (cuprammonium ion); antimony in presence of tartrate (tartar emetic); complex cyanides. In such cases the metallic radical can usually be removed, if necessary, by passing H_2S through the solution acidified with acetic acid, and, after filtering, removing the H_2S by boiling; but volatile acids (HCN) may be lost during the process, and in presence of oxidising agents (such as nitrate or chlorate) sulphate may be formed by oxidation of the H_2S.

2. The sodium carbonate must be carefully tested for chloride and sulphate, which are often present as impurities.

1. Silver Nitrate Test.

To about 5 c.c. of the solution[1] add dilute HNO_3 in slight excess, and boil to expel CO_2, SO_2, etc. If a precipitate forms and does not redissolve when more HNO_3 is added, it may be sulphur (from thiosulphate), silicic acid, etc. Filter if necessary, and cool.

Add a few drops of $AgNO_3$; if a precipitate forms, add more $AgNO_3$ until precipitation is complete. Note the colour of the precipitate, shake vigorously, and filter:—

Precipitate.—	AgCl, AgCN, AgCNS	(*White, curdy*).
	$Ag_4Fe(CN)_6$ . .	(*White, flocculent*).
	AgBr	(*Pale yellow, curdy*).
	AgI	(*Yellow, curdy*).
	$Ag_3Fe(CN)_6$ . .	(*Red-brown, flocculent*)

AgCN (unlike AgCl) is not darkened by exposure to sunlight

(*a*) Warm a portion of the precipitate with NH_4OH AgI and $Ag_4Fe(CN)_6$ are insoluble in NH_4OH. If the precipitate is not entirely soluble in NH_4OH, filter, and add excess of HNO_3 to the filtrate: AgCl, AgBr, AgCN AgCNS, and $Ag_3Fe(CN)_6$ are reprecipitated.

(*b*) In a covered porcelain basin mix a portion of the precipitate with concentrated HNO_3 and heat on the steam-bath for half an hour:—

AgCl, AgBr, and AgI are not appreciably attacked.
AgCN and AgCNS are slowly decomposed.
$Ag_4Fe(CN)_6$ (white) is immediately converted into $Ag_3Fe(CN)_6$ (red-brown), which dissolves very slowly

Filtrate.—Add NH_4OH cautiously, without shaking. The following may be precipitated at the neutral zone where

[1] Unless the contrary is stated, the "solution" used for all special tests is either—

(*a*) An aqueous solution of the substance (if only Na, K, and NH_4 salts are present); or
(*b*) The "sodium carbonate extract," prepared as described by boiling the substance with sodium carbonate and filtering. Before using this solution for any test, the excess of sodium carbonate must be decomposed by adding an appropriate acid.

the liquids meet:—Ag_3PO_4 and Ag_3AsO_3 (yellow); Ag_3AsO_4 (brown); Ag_2CrO_4 (crimson).

If $AgNO_3$ gives no precipitate in presence of HNO_3 (chloride, bromide, iodide, cyanide, ferrocyanide, ferricyanide, and thiocyanate absent), add NH_4OH to the same solution in the manner indicated here.

2. Barium Chloride Test.

Acidify about 3 c.c. of the solution with HCl, care being taken to avoid a large excess of acid. Boil and, if necessary, filter. Add several drops of $BaCl_2$ solution, and boil; if no precipitate forms, cool, and set aside for at least five minutes. If a white, powdery (crystalline) precipitate forms, sulphate is present. (Make certain that the solution is acid, and that the precipitate does not dissolve on addition of several drops of HCl.) Note that $BaSO_4$ separates very slowly from a dilute solution, *i.e.*, if only a small amount of sulphate is present.

3. Calcium Chloride Test.

Acidify about 3 c.c. of the solution with acetic acid, boil, and (if necessary) filter. To the warm solution add $CaCl_2$: if a precipitate forms, it may consist of—

CaC_2O_4 (*white, crystalline*).
CaF_2 (*white, opalescent*).

If fluoride is present (usually detected in the preliminary examination), filter the precipitate, and wash. Dissolve the precipitate by pouring hot, dilute H_2SO_4 into the filter, and to the hot solution add dilute $KMnO_4$ solution, drop by drop. The $KMnO_4$ is reduced and decolourised if oxalate is present.

Note.—In presence of much sulphate it is safer to use $CaSO_4$ solution (in excess) for this test instead of $CaCl_2$—in case a possible precipitate of $CaSO_4$ is mistaken for CaC_2O_4.

4. Cyanide, Ferrocyanide, Ferricyanide, Thiocyanate.

The preliminary examination and the silver nitrate test will have indicated what confirmatory or supplementary tests are necessary.

Cyanide. — Confirm by the "Prussian-blue" test:— To a portion of the solution add NaOH and a little $FeSO_4$ solution, boil, and acidify with HCl. In presence of cyanide, ferric ferrocyanide ("Prussian blue") is formed.

If ferro- or ferri-cyanide is present, proceed as follows:— To a portion of the solution add a little solid $NaHCO_3$ and lead CO_2 (from a Kipp's generator) through the warm liquid, and then pass the escaping gas with any HCN into a few drops of yellow ammonium sulphide (Fig. 2, p. 2). Rinse the ammonium sulphide into a basin, evaporate nearly to dryness, acidify with HCl, and test for *thiocyanate* by adding a drop of $FeCl_3$.

Ferrocyanide, Ferricyanide, Thiocyanate. — Acidify the solution with HCl and add to separate portions (i) ferric chloride, (ii) ferrous ammonium sulphate (fresh solution). If necessary, examine further as follows:—

(*a*) For *ferricyanide*, in presence of ferrocyanide. Acidify the solution with HCl, add KI, and warm: iodine is liberated.

(*b*) For *thiocyanate*, in presence of ferrocyanide. To the *neutral* solution[1] add $Zn(NO_3)_2$, warm, and filter. Test the filtrate for thiocyanate with HCl and $FeCl_3$.

(*c*) For *thiocyanate*, in presence of iodide.[2] Acidify the solution with HNO_3, add $AgNO_3$ in slight excess, warm, filter, and wash. Warm the precipitate with NH_4OH (AgI is insoluble), and filter. To the filtrate add H_2S, and filter the Ag_2S. To this filtrate add a few drops of Na_2CO_3, evaporate to a small volume, and test for thiocyanate with HCl and $FeCl_3$.

5. Chloride, Bromide, Iodide.

The preliminary examination and the silver nitrate test will have indicated what supplementary tests are necessary.

[1] Acidify the "sodium carbonate extract" with HNO_3, and boil. Neutralise carefully with NH_4OH.

[2] Iodide interferes with the ferric chloride test for thiocyanate, iodine being liberated:—$FeCl_3 + KI = FeCl_2 + KCl + I$.

In Absence of Cyanide, Ferrocyanide, Ferricyanide, and Thiocyanate.

(*a*) Test for iodide and bromide as follows:—

Acidify a portion of the solution with dilute H_2SO_4, add about 1 c.c. of chloroform and 1 drop of Cl_2-water. Shake vigorously. The chloroform layer becomes violet if iodide is present, and brown if bromide (but no iodide) is present.

If iodide is present, add more Cl_2-water gradually, and shake vigorously after each addition. The violet colour due to iodine (which is oxidised to iodic acid) gradually disappears, and in presence of bromide further addition of Cl_2-water liberates bromine, which dissolves in the chloroform to give a brown solution. With excess of Cl_2-water the colour vanishes owing to the formation of BrCl.

This method may fail to detect bromide in small quantity if much iodide is present, and in that case it is better to proceed as follows:—Acidify a portion of the solution with acetic acid, add H_2O_2, and expel the liberated iodine by boiling the solution in a basin. Transfer the solution to a test-tube, and cool. Test for bromide by adding a few drops of Cl_2-water and shaking with chloroform.

(*b*) If iodide *and* bromide are present, test for chloride as follows:—Acidify the solution with acetic acid, add H_2O_2, and expel iodine by boiling in a basin. Then add to the solution one-third of its volume of concentrated HNO_3 and expel bromine by boiling. Add more HNO_3 (1 vol. acid + 3 vols. water) at intervals, and continue boiling until the solution is colourless. Cool, and test for chloride with $AgNO_3$. (Iodides and bromides may contain sufficient chloride to give an opalescence here.)

The above procedure may be readily modified if only iodide *or* bromide is present.

In Presence of Cyanide, Ferrocyanide, Ferricyanide, or Thiocyanate.

To a portion of the *neutral* solution add $Zn(NO_3)_2$ (which precipitates cyanide, ferrocyanide, and ferricyanide), warm, and filter.

(*a*) If thiocyanate is absent, examine this filtrate for chloride, bromide, and iodide as described above (p. 63).

(*b*) If thiocyanate is present, proceed as follows:—To this filtrate add dilute HNO_3 and $AgNO_3$ in slight excess, warm, filter, and wash (neglect the filtrate). Heat the precipitate with concentrated HNO_3 on the steam-bath in a covered basin for half an hour. (AgCNS is decomposed.) Dilute, filter, and wash. Reduce the precipitate by warming it for a few minutes with dilute H_2SO_4 and a piece of zinc. Filter, and test the filtrate for chloride, bromide, and iodide as already described.

6. Nitrate.

This radical may have been detected in the preliminary examination (sublimation tube, and interaction with concentrated H_2SO_4). Its presence must be confirmed, as follows:—

(*a*) "Brown ring" test:—Acidify 2 c.c. of the solution with dilute H_2SO_4, and add about 5 c.c. of concentrated $FeSO_4$ solution. Then pour concentrated H_2SO_4 slowly down the side of the tube *so as to form a separate layer.* If nitrate is present, a brown coloration forms just above the interface. The coloration disappears on heating, and NO is liberated. Nitrite gives the same reaction, and many substances interfere with the test, especially iodide, bromide, chromate, and chlorate.

(*b*) If iodide, bromide, or chlorate is present, test for nitrate by reducing to ammonia with zinc dust in presence of very dilute H_2SO_4 (p. 15). If the original substance contains ammonium salts, boil the solution in a small flask with NaOH until NH_3 is no longer evolved. Add dilute H_2SO_4 sufficient to make the solution faintly acid; then add zinc dust and set aside for five minutes. Finally, add NaOH until alkaline, boil, and test for NH_3.

(*c*) If chromate is present, acidify the solution with dilute H_2SO_4, and add sufficient H_2SO_3 to reduce the chromate to chromic sulphate, *i.e.* to produce a pure green colour. Remove Cr by adding NH_4OH, boiling, and filtering. Evaporate the filtrate to a small volume, acidify with dilute H_2SO_4, and test for NO_3 by the "brown ring" test.

(*d*) If nitrite is present, test for NO_3 by the brucine reaction;—Evaporate about 2 c.c. of the solution to dryness, mix with 2 c.c. of concentrated H_2SO_4, and add a few milligrams of brucine (or 1 c.c. of a solution containing 0·2 gram of brucine in 100 c.c. of concentrated H_2SO_4). If nitrate is present, a red coloration is obtained; this quickly changes to orange, and then slowly becomes yellow or greenish-yellow.

7. Arsenite, Arsenate, Phosphate.

See evidence obtained during the analysis for the metallic radicals, p. 57.

(*a*) The silver nitrate test (p. 60) may have given useful indications.

(*b*) *Ammonium Molybdate Test for Phosphate and Arsenate.*—Add excess of HNO_3 to the solution; then add about 1 c.c. (or more if no precipitate is obtained with this amount) of this solution to about 5 c.c. of ammonium molybdate, and warm and then boil. *Phosphate* and *arsenate* give yellow precipitates—in the case of arsenate the precipitate forms more readily on boiling, but this difference cannot be relied upon as a distinguishing test. (Note 1.)

(*c*) *Separation of Arsenite, Arsenate, and Phosphate.*—Acidify the solution with HCl; add NH_4OH until alkaline and then magnesia mixture ($MgCl_2+NH_4Cl+NH_4OH$); shake vigorously and filter. (If no precipitate forms, arsenate and phosphate are absent.)

Filtrate. — Acidify with HCl and saturate with H_2S: a yellow precipitate (As_2S_3) indicates AsO_3'''.

Precipitate. — $MgNH_4AsO_4$, $MgNH_4PO_4$: — Wash carefully; dissolve in moderately concentrated HCl, add 1 c.c. of NH_4I solution, boil, and saturate with H_2S: a yellow precipitate (As_2S_3+S) indicates AsO_4'''. Boil, and filter. Make certain that precipitation of arsenate is complete. Expel H_2S from the filtrate, and test for phosphate with ammonium molybdate. (Note 2.)

Notes.—1. This test for phosphate is always made after removal of arsenic in Group II. (see p. 44).

2. Phosphate having been identified in the course of the examination for metallic radicals, this separation is necessary only for the purpose of identifying arsenite in presence of arsenate.

8. Acetate.

If present, acetate is usually detected in the preliminary examination. It may be confirmed by tests (*a*) or (*b*) in absence of interfering substances, or by test (*c*).

(*a*) To the *neutral* solution add several drops of "neutral" (aqueous) $FeCl_3$ solution. A red-brown coloration is produced, and basic ferric acetate is precipitated on boiling. Sulphite, thiosulphate, iodide, and tartrate interfere.

(*b*) To 1 c.c. of alcohol add 1 c.c. of concentrated H_2SO_4, and cool. Add a little of the substance to this mixture and warm the tube in boiling water. In presence of acetate, ethyl acetate (characteristic odour) is formed. If amyl alcohol (1 drop) is used instead of ethyl alcohol, amyl acetate (odour of Jargonelle pear essence) is formed.

(*c*) Heat in a dry tube a small quantity of the substance with Na_2CO_3 and a *minute* amount of As_2O_3. *Very poisonous* cacodyl oxide, $(CH_3)_2As.O.As(CH_3)_2$, recognised by its repulsive odour, is formed.

9. Tartrate.

The presence of organic acidic radicals ought to be detected, as a rule, in the preliminary examination. Confirm tartrate as follows:—

(*a*) In a porcelain basin mix a small quantity of the substance with twice its bulk of resorcinol and about ·2 c.c. of concentrated H_2SO_4. Heat the mixture gently. In presence of tartrate, a bright red coloration is produced.

(*b*) Acidify a portion of the solution with HCl (to decompose carbonate), add excess of NaOH and 2 drops of $CuSO_4$. In presence of tartrate, a blue solution (but no precipitate) is obtained. Ammonium ion, arsenite, and possibly other radicals interfere.

(*c*) *Silver-mirror Test.*—As the presence of other acids generally interferes, proceed as follows:—Acidify a portion of the solution with acetic acid and evaporate to a very small volume. Add a drop of acetic acid and an equal volume of concentrated potassium acetate solution. Stir, and set aside. If no precipitate ($KHC_4H_4O_6$) forms, add a little alcohol. Filter, wash the precipitate with dilute

alcohol, and dry to remove the alcohol. Dissolve the precipitate in the minimum amount of dilute NaOH (use a perfectly clean test-tube). Add $AgNO_3$ in slight excess, and then very dilute NH_4OH, drop by drop, until the precipitate is *nearly* redissolved. Heat the solution by placing the test-tube in hot water.

10. Borate.

In the preliminary examination little evidence is obtained regarding borate except possibly the characteristic intumescence (swelling up) observed when water of hydration is expelled from alkali borates, such as borax, by heat.

(*a*) *Turmeric Paper Test.*—Acidify the solution *slightly* with HCl and partly immerse a strip of turmeric paper in it, and then dry the paper. If boric acid is present, the paper assumes a reddish colour. Substances which interfere with this test include ferric salts, iodides, chromates, and chlorates.

(*b*) *Flame Coloration Test.*—On a watch-glass mix a small quantity of the substance with CaF_2 and 1 drop of concentrated H_2SO_4. On a looped platinum wire hold some of the paste thus formed close to but not touching the base of a Bunsen flame. If borate is present, boron fluoride volatilises and colours the flame green. If care be taken, barium and copper salts do not interfere with this test.

With regard to the detection of borate in presence of silicate (borosilicate), see p. 77.

11. Fluoride.

The presence of fluoride may have been indicated in the preliminary examination. Confirm fluoride by the glass etching test (p. 16). This test may fail, however, if silicate is present, because the substance may not be decomposed by H_2SO_4, or because SiF_4 may be liberated instead of HF. (Compare p. 77.)

12. Silicate.

This is commonly met with only in minerals and metallurgical products (see p. 75). Its presence is usually detected in the preliminary examination by the metaphosphate bead test. See also under "Examination of Substances insoluble in Acids," p. 71.

EXAMINATION OF SUBSTANCES INSOLUBLE IN ACIDS.

If the substance cannot be dissolved completely by boiling with concentrated HCl, HNO_3, or aqua regia, and then diluting with an equal volume of water, filter while hot and wash the insoluble residue thoroughly with hot water. Cool the filtrate and washings ($PbCl_2$ may be precipitated on cooling), and examine for metallic radicals as usual.

The insoluble substances most frequently met with include the following:—

White.

$BaSO_4$, $SrSO_4$, $PbSO_4$.
SiO_2, many silicates.
Al_2O_3 (*natural or ignited*).
SnO_2 („ „).
Sb_2O_4, Sb_2O_5.
CaF_2.
AgCl (*violet after exposure to light*).

Pale Yellow.

AgBr (*violet after exposure to light*).

Yellow.

AgI.
Sulphur.

Bronze (*with metallic lustre*).

SnS_2 (mosaic gold).

Green.

Cr_2O_3 (*ignited*).

Blue.

$Fe_4[Fe(CN)_6]_3$.

Brown.

$PbCrO_4$ (*fused*).
$Cu_2Fe(CN)_6$.

Dark Red.

Fe_2O_3 (*ignited*).

Black.

Carbon (graphite, charcoal, etc.)
SiC (carborundum).
Fe_3O_4 (magnetite).

The general character of the original substance, together with the results of the preliminary examination, may afford a guide as to the probable nature of the insoluble residue. The appearance of the latter—its colour more particularly—may reveal the presence or indicate the absence of many of the above substances, and in some cases a few simple dry-way tests may suffice to identify it. In other cases it may be necessary to bring the substance into solution after decomposing it by one of the following methods:—

1. Fusion with Na_2CO_3: for $BaSO_4$, $SrSO_4$, SiO_2, silicates.
2. Fusion with Na_2CO_3+S: for SnO_2, Sb_2O_4, Sb_2O_5.

3. Fusion with NaOH: for acidic oxides (SnO_2, Sb_2O_4, SiO_2, Al_2O_3).
4. Fusion with $K_2S_2O_7$: for basic oxides (Fe_2O_3, Cr_2O_3, Al_2O_3).
5. Reduction with Zn and dilute H_2SO_4: for AgCl, AgBr, AgI.
6. Boiling with NaOH solution: for $PbSO_4$, $PbCrO_4$, ferrocyanides.

Complex mixtures of essentially different types of insoluble substances are rarely met with in practice. Where a mixture has to be analysed, a combination of the following methods of attack, whereby the various constituents are successively eliminated or identified, may be readily devised.

PROCEDURE.

Note the general appearance and colour of the substance very carefully. Dry it in the steam-oven, or by placing the unfolded filter paper on two glass rods laid on wire gauze and heating very gently with a small flame. Examine it further as described below.

The Substance is Coloured.

1. The following can usually be identified by colour :—

Cr_2O_3 : Confirm by borax and sodium carbonate beads.

Fe_2O_3 : Confirm by borax bead. Fuse with $K_2S_2O_7$[1] c platinum foil: dissolve the residue in dilute H_2SC and test the solution for Fe.

SnS_2 : (Is slowly decomposed by aqua regia.)

(*a*) Reduce on charcoal (match test) and examine the residue for tin globules and for sulphide (hepar test, p. 33).

[1] Potassium pyrosulphate is obtained by fusing potassium hydrogen sulphate until water is no longer given off—

$$2KHSO_4 = K_2S_2O_7 + H_2O.$$

On further heating (with the substance under examination), the pyrosulphate is converted into normal sulphate and SO_3—which is the active agent in effecting decomposition of the substance.

$$K_2S_2O_7 = K_2SO_4 + SO_3.$$

(*b*) Mix with five times its bulk of Na_2CO_3+S (equal parts) and heat strongly in a covered crucible. Cool, and dissolve in water. The solution contains sodium thiostannate which may be readily identified.

Sulphur: Is usually unmistakable. Heated on a crucible lid, it melts and burns—odour of SO_2.

Prussian blue: Boil with NaOH, and filter: examine the precipitate for Fe and the filtrate for ferrocyanide.

2. A yellow substance may be—

(*a*) Sulphur: Examine as above.

(*b*) AgBr or AgI: Warm for a few minutes with Zn dust and dilute H_2SO_4. Filter. Examine the filtrate for bromide and iodide. Dissolve residue in the HNO_3 and test for Ag.

3. A brown substance may be (*a*) $PbCrO_4$, or (*b*) $Cu_2Fe(CN)_6$. Boil with NaOH:—

$PbCrO_4$ dissolves: add excess of HCl and examine for Pb and Cr as usual.

$Cu_2Fe(CN)_6$ is decomposed like Prussian blue (above).

4. A black substance may be—

(*a*) Carbon: Heat on platinum foil in blowpipe flame: carbon glows and burns away. Graphite, however, burns with difficulty: fuse it with KNO_3 on platinum foil and test the residue for carbonate.

(*b*) Fe_3O_4: Is magnetic. Confirm as for Fe_2O_3.

(*c*) SiC: Characterised by extreme hardness. Fuse with NaOH in a silver or nickel crucible, and examine the residue for silicate and carbonate.

The Substance is White.

1. Moisten a small portion of the substance with ammonium sulphide. If it becomes black, it may be $PbSO_4$ or AgCl.

AgCl, *which darkens on exposure to light*, dissolves in NH_4OH; it may also be identified by reduction with Zn and H_2SO_4 (compare AgBr, above).

$PbSO_4$ dissolves in concentrated ammonium acetate

solution. Test the solution so obtained for Pb by adding H_2SO_4; and for SO_4 with HNO_3 and $Ba(NO_3)_2$.

2. Heat a little of the substance on a platinum wire loop in the *reducing* flame. Moisten in 1 drop of concentrated HCl on a watch-glass, and try the flame coloration. Ba and Sr are thus identified. To confirm:—

Boil the substance with a little concentrated Na_2CO_3 solution for several minutes and filter.

Precipitate.—Wash, pour hot dilute acetic acid over it, and test the solution for Ba and Sr in the usual way.

Filtrate.—Add excess of dilute hydrochloric acid and test for SO_4 with $BaCl_2$.

$BaSO_4$ and $SrSO_4$ are more easily decomposed by fusing with Na_2CO_3 on platinum foil. The fused mass (and the foil) is then boiled with water, filtered, and the precipitate and solution examined as above.

3. Fuse the substance in a metaphosphate bead. SiO_2 and silicate are identified in this way. SnO_2 "dissolves" very slowly in a metaphosphate bead, and disappears, as a rule, only on prolonged heating. It may thus be confused with SiO_2.

To confirm SnO_2:—In a nickel (or silver) crucible melt a small piece of NaOH (not more than ½ inch stick) together with 2 to 3 drops of water. To the molten soda add the insoluble substance and keep the mixture fused until the substance dissolves. Allow to cool. Add 10 c.c. of water, warm until the fused mass is disintegrated, dilute, and filter. Test the filtrate for Sn (stannic) as follows:—

(*a*) Add HCl until acid (note precipitation of stannic hydroxide, soluble in excess of acid); reduce with Fe by warming with a nail for a few minutes; then add $HgCl_2$.

(*b*) Acidify with HCl and add H_2S: SnS_2 is precipitated —soluble in NaOH.

To confirm SiO_2:—Fuse with Na_2CO_3 on platinum foil (SiO_2 causes effervescence). Boil the fused mass with water —it will dissolve completely if the insoluble substance was SiO_2 only. Filter if necessary, add excess of HCl to the filtrate, and evaporate to complete dryness. (SiO_2 is

thus rendered insoluble again.) Moisten residue with HCl, add a little water, warm, and filter. Examine any insoluble residue in a metaphosphate bead.

The analysis of an insoluble silicate is described on p. 77.

4. If a fluoride was found in the original substance, test the insoluble substance for fluoride. Also, fuse the insoluble residue with Na_2CO_3 and a little pure silica; boil the fused mass with water, filter, and wash the residue; examine it for Ca.

5. Sb_2O_4 and Sb_2O_5. Usually met with when alloys containing Sb are disintegrated with HNO_3. May be identified after fusion with NaOH as described for SnO_2, or as follows:—Mix the finely powdered substance with five times as much Na_2CO_3+S (equal parts) and heat the mixture in a *covered* porcelain crucible for about ten minutes. Cool. Boil the crucible and contents with water, and filter. Acidify the filtrate with HCl: Sb_2S_5 is precipitated and may be readily identified.

6. Al_2O_3. Gives a blue infusible mass when heated with a drop of $Co(NO_3)_2$ on charcoal (p. 32), but silicates, borates, etc., give a similar result.

Fuse with $K_2S_2O_7$ on platinum foil. Dissolve the residue in dilute H_2SO_4 and examine the solution for Al.

ANALYSIS OF METALS AND ALLOYS.

Nitric acid is usually the best solvent for metallic substances. It has a very feeble action, however, on aluminium and some aluminium alloys, for which hydrochloric acid should be employed. Hydrochloric acid should be avoided in the case of alloys likely to contain phosphorus and arsenic, since these elements are evolved as hydrides and may escape detection. Tin and antimony are not "dissolved" by concentrated nitric acid, but are converted into insoluble metastannic acid and antimonic acid. Aqua regia must be used for gold and platinum.

PROCEDURE.

Note the colour of a freshly exposed surface of the metal, and the physical characteristics generally. If the metal is soft, roll or hammer it into a thin strip; if it is hard or brittle, obtain it in the form of clean borings or cut it into small pieces.

Use from 0·2 to 0·3 gram. Add 5 c.c. of water and then 5 to 10 c.c. of concentrated HNO_3, and warm gently in a porcelain basin as long as any action continues. Evaporate *nearly* to dryness (preferably on the steam-bath), add 20 c.c. of water, and warm again.

1. Alloys containing no Au, Pt, Sn, or Sb usually dissolve completely. Examine the solution for metallic radicals and for PO_4''' as usual. (Common alloys contain no Ca, Sr, Ba, Na, or K.)

2. A black residue may be Au or Pt (soluble in aqua regia), C or Si.

3. A white (or greenish-white) residue[1] is probably metastannic or antimonic acids, and may contain stannic phosphate and arsenate, together with small amounts of other oxides (PbO, CuO, Bi_2O_3). Filter, and wash the insoluble residue.

Filtrate.—Examine for metallic radicals (except Sn and Sb) as usual.

[1] A small, white, *flocculent* residue may be silicic acid; test in a metaphosphate bead.

Insoluble Residue.—(*a*) Boil with 5 c.c. of concentrated HCl and then dilute with 10 c.c. of water.[1] Examine the solution for the radicals of Group II., and for PO_4''';

or,

(*b*) Mix with 5-10 c.c. of yellow ammonium sulphide[2] and boil for a few seconds. (Stannic, antimonic, and arsenic acids dissolve, forming thiosalts; other metallic oxides remain undissolved as sulphides.) Filter, and wash.

Precipitate.—This may usually be neglected. It consists of sulphides of the metallic radicals found in the nitric acid solution of the alloy, together with (as a rule) some undecomposed Sn and Sb oxides.

Filtrate. — Acidify cautiously with HCl (add the acid from a test-tube, and not from the reagent bottle), and filter.

Precipitate.—Examine for Sn, Sb, and As.

Filtrate.—Boil free from H_2S and test for PO_4''' with $(NH_4)_2MoO_4$.

[1] As a rule, the residue dissolves quite readily. If not, use method (*b*).

[2] This reagent is prepared by shaking finely powdered sulphur (2 grams) with ordinary ammonium sulphide (1 litre).

ANALYSIS OF MINERALS, GLASSES, SLAGS, ETC.

A mineral is commonly either an oxide, sulphide, carbonate, silicate, sulphate, phosphate, fluoride, chloride, or borate. The following are typical examples:—

Oxides: Quartz (SiO_2); hæmatite (Fe_2O_3); cassiterite (SnO_2).

Sulphides: Pyrite (FeS_2); galena (PbS); cinnabar (HgS).

Carbonates: Calcite ($CaCO_3$); dolomite ($CaCO_3$, $MgCO_3$).

Silicates: Felspar, mica, garnet (complex aluminous silicates); hornblende, olivine, talc (essentially magnesian silicates).

Sulphates: Barytes ($BaSO_4$); gypsum ($CaSO_4$, $2H_2O$).

Phosphates: Chlor-apatite [$3Ca_3(PO_4)_2$, $CaCl_2$]; fluor-apatite [$3Ca_3(PO_4)_2$, CaF_2].

Fluorides: Fluorspar (CaF_2); cryolite ($3NaF$, AlF_3).

Borates: Borocalcite (CaB_4O_7, $6H_2O$); tourmaline (essentially alumino-borosilicate).

Pure specimens of minerals are rare. Associated with the main constituents there are almost invariably much smaller amounts of other elements; and most specimens are contaminated with more or less adventitious matter or gangue. In the report of the analysis it is most important to distinguish clearly between the main constituents and those present in small amounts.

PRELIMINARY EXAMINATION.

Endeavour to ascertain, if possible, to which of the above groups the mineral belongs.

1. Examine the mineral closely. Many minerals can be readily identified by their physical characteristics alone.

2. Grind the mineral to a powder. Most minerals must be very finely powdered before proceeding with the analysis (p. 22).

3. Try the usual preliminary tests. Test carefully for carbonate, sulphide, silicate, and fluoride. Sulphides like

FeS_2, which are not decomposed by HCl alone, yield H_2S on adding a little zinc dust.

4. Boil the substance gently with concentrated HNO_3 (separation of sulphur from a sulphide may be observed); dilute, and filter. Test portions of the filtrate as follows:—

(*a*) For phosphate (if arsenic is absent) with $(NH_4)_2MoO_4$.
(*b*) For sulphate (if sulphide is absent) with $BaCl_2$.
(*c*) For chloride with $AgNO_3$.

If arsenic is present, test for phosphate in the systematic analysis after removal of Group II.

If sulphide is present, test for sulphate in the Na_2CO_3 extract as usual.

5. Test for borate by the flame coloration.

SYSTEMATIC ANALYSIS.

In preparing a solution for analysis be guided by the results of the preliminary examination.

Mineral sulphides are best decomposed by concentrated HNO_3 or aqua regia kept near the boiling-point. (Nothing is gained by vigorous boiling.) The sulphur which separates as a spongy mass is often black at first, but becomes yellow on continued heating and is easily identified.

Some silicates (zeolites) are decomposed by HCl, with separation of gelatinous silica. Most silicates are practically unattacked by acids, and must be decomposed as described in detail below.

Barytes, fluorspar, cassiterite and some other mineral oxides are practically insoluble in acids.

Separate the soluble and insoluble portions by filtration, and examine the solution and insoluble residue in the usual way. As practically all minerals are liable to contain at least a small amount of silica or silicate, the solution may contain dissolved silica and must therefore be evaporated to dryness prior to the precipitation of Group III., in order to render the silica insoluble.

All the acidic radicals likely to be present are usually detected in the preliminary examination, or in the examination of the insoluble residue. If necessary, the substance

may be boiled with Na_2CO_3 solution, and the extract examined for sulphate.

Analysis of Insoluble Silicates (*natural silicates, artificial glasses, porcelain, etc.*).—Grind the substance very finely. Mix about 0·5 gram with about 3 grams of dry Na_2CO_3 (or fusion mixture—$Na_2CO_3+K_2CO_3$) and heat the mixture in a platinum crucible (or on platinum foil), gently at first, and then strongly with the blowpipe, until effervescence ceases and quiet fusion is attained.

Cool. Boil the fused mass with water until it is disintegrated. Filter a small portion and reserve the filtrate for acidic radicals (see below). To the main portion add HCl in slight excess, and evaporate to complete dryness to render SiO_2 insoluble. Moisten the residue with concentrated HCl, add a little water, and warm. Filter, and wash with hot water.

Residue.—This is mainly SiO_2. (It invariably contains traces of Al_2O_3, Fe_2O_3, and TiO_2, and may contain $BaSO_4$.)

Filtrate.—Examine it for metallic radicals, except Na and K.

Test the aqueous extract of the fusion (obtained as above) for sulphate and chloride, and also for borate and fluoride if they have not been already detected. The flame test for borate, using the original substance, may be unreliable, as some borosilicates are not decomposed by concentrated H_2SO_4.

Test for fluoride as follows:—Evaporate a portion of the aqueous extract to a small volume, acidify with acetic acid, and, if silicic acid separates, filter. Add $CaCl_2$ to the filtrate, and, if a precipitate (possibly CaF_2) forms, collect it on a small filter, wash and dry it, and test it for fluoride in the usual manner.

Detection of the Alkali Metals.—(*a*) Mix the silicate with ammonium fluoride and heat the mixture on a looped platinum wire. Moisten with HCl, and examine the flame coloration for Na, K, and Li (use the spectroscope).

(*b*) On a small piece of "ashless" filter paper mix a small quantity of the silicate with a pinch, (20 mgrms.) of Mg powder. Fold into a small packet and wrap a piece of thin iron wire round it. Ignite (kindle) the paper

and allow the paper and contents to burn. Place the residue on a watch-glass, moisten with a drop of concentrated HCl, and examine the flame coloration.

(*c*) A more complete analysis may be made as follows:—Mix the silicate with 5 c.c. of HF (or a little NH_4F) and 2 c.c. of moderately concentrated H_2SO_4 in a platinum crucible. Heat on the steam-bath and afterwards with a small flame until most of the H_2SO_4 is expelled.[1] Moisten the residue with concentrated HCl, add water, warm, and filter (an insoluble residue may be $BaSO_4$ or $PbSO_4$). Examine the solution for metallic radicals, including Na, K, and Li.

[1] Carry out the evaporation in a good draught, and do not inhale any HF.

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